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SURVEY OF ANTHOXANTHINS—PART I

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Flavonoids occur widely in the plant kingdom, and their study may probably be more freely used than hitherto in genetics, plant classification and physiology. In this respect they should be considered to be as important as anthocyanins, whose analysis in small quantities of plant materials has been carefully worked out by Robinson and collaborators.[1] The use of paper chromatography for the identification of anthocyanins in petal extracts has been investigated by Batesmith,[2] using the linear flow method. In the case of anthoxanthins, the evolution of a satisfactory chemical micromethod has not been possible so far. The more promising method of paper chromatography has been studied by Wender and collaborators,[3] again using the linear migration method. They have recorded the Rf values of a large number of anthoxanthins belonging to different groups, aglycones and glycosides, using various solvent combinations and fluorescence and chromogenic sprays. But its dependability for analysing naturally occurring mixtures has not been investigated in detail. It is the purpose of the present work, to examine convenient and quick methods of analysing plant materials in small quantities and applying them for the survey of anthoxanthins. These occur usually as mixutres which are sometimes complex. Complete analysis has rarely been effected; though by employing the method of fractionation adopted by Seshadri and co-workers,[4] it is possible to get more information than by earlier procedures, still the results could not be taken as complete. Paper chromatography has now been used for diagnostic purposes and the results verified by regular methods of fractionation. They corroborate each other and indicate that the paper chromatography is quite dependable.

Among the methods of paper chromatography the circular one described by Rao and Beri[5] for sugars is found to work quite satisfactorily. Its special virtue is quickness. In the case of flavonols which are chosen in the first instance for study, there is no need to develop the rings by means of chromogenic sprays, since they are sufficiently coloured yellow to indicate their location.

To begin with, authentic samples of pure flavonols have been prepared synthetically, chromatographed and the circular Rf values determined. This choice of substances is based on their occurrence in nature, since the results are intended to be used for the study of natural sources. Each flavonol gives its own zone with a fixed Rf value. There is no difficulty of multiple zones occurring as reported in certain cases by others.[6] Next extracts from plant sources have been examined; there is no difficulty in identifying the components from the rings. For purposes of verification, extraction and separation of flavonoid mixtures have been effected using methods of fractional precipitation and crystallisation and also chromatographic separation using alumina. It may be recorded here that these fractionation methods have not only corroborated the results of filter-paper chromatography, but indicate that with greater precaution, the existence of various entities in plant materials could be independently proved. These tested materials could therefore be used as standards of reference in case pure synthetic samples of the flavonols are not available for comparison. Since the Rf values are liable to vary with the conditions of t xperiment, it is essential that this comparison should be carefully done usin ure synthetic flavonol samples or plant sources whose composition has been definitely established. Our results indicate that flavonoids in general, occur as mixtures of two or more entities, and it is rare to find them single. Further, in the large majority of cases, quercetin is an invariable component.

For the present survey, we have laid particular emphasis on the identification of the aglycones and their separation, rather than on the glycosides in which form they may occur. We feel that this procedure is more dependable and more useful. However, some information regarding the nature of the glycosides present could be obtained even with small quantities by the study of reactions with lead acetate and zinc and concentrated hydrochloric acid (Pew's reaction).[7] The following typical examples will illustrate the general methods of fractionation that have been adopted.

1. Moringa Flowers (*Moringa pterygosperma*)

Various parts of this tree, leaves, flowers and pods have been used as food and as drug, and therefore have been investigated carefully. But so far the existence of flavonoids in the flowers has not been recorded.[8] In the course of the present work two varieties of Moringa trees have been chosen, one the 'sweet' variety and the other the 'bitter'. Both have been found to contain rather low quantities of a flavonoid mixture, circular chromatography indicating the presence of two, a pentahydroxy and a tetrahydroxy flavone, closely agreeing with quercetin and kæmpferol res-

pectively. The separation of the mixtures has been carried out using their full methyl ethers and passing them through a column of alumina. Kæmpferol tetramethyl ether is washed out first and quercetin ether later.

2. Neem Flowers

The flowers of the neem tree were examined by Mitra and Siddiqui[9] and they reported the isolation in poor yield of kæmpferol. In our experiments we find that the fresh flowers contain a high percentage of extractable flavonoids, about 0·5%, which will work out to be about 1·5% on air-dried matter. But there seems to be considerable loss of pigments when the flowers are sun dried and stored. Still about 1% yield can be secured, if the flowers are moistened first with water, allowed to stand for a few hours and then alcohol added for extraction. Chromatography indicated the presence of three compounds, corresponding to hexa-, penta-, and tetra-hydroxy flavones agreeing with myricetin, quercetin and kæmpferol. For effecting the separation, the total pigment in aqueous alcoholic solution, is treated with excess of neutral lead acetate and after filtering off the neutral lead salt, excess of basic lead acetate added. The portion obtained by the decomposition of the neutral lead salt is fractionated by the acetate method. Quercetin is obtained as the main component and myricetin as the minor. In the basic lead salt fraction kæmpferol happens to be the only entity and is readily obtained as the free hydroxy flavone.

3. Indian Podophyllum (*Podophyllum emodi*)

Podwyssotski[10] was the earliest to isolate a yellow colouring matter from the American Podophyllum (*Podophyllum peltatum*). He called this podophylloquercetin. Kursten[11] extending the work of Podwyssotski showed, from an examination of the acetyl, and benzoyl derivatives and also the methyl ether that podophylloquercetin was not identical with quercetin from quercitron bark. Obviously it was a mixture. Later Dunstan and Henry[12] made a comparative study of both Indian podophyllum (*P. emodi*) and *P. peltatum*. They established the presence of quercetin in both these but only after considerable purification they could make sure of its identity. In the recent work of Seshadri and Subramanian[13] quercetin has been obtained more readily pure. In the present analysis using filter-paper chromatography the flavonoid part of this resin yields two distinct zones, one corresponding to a tetra-(kæmpferol) and the other corresponding to a penta-hydroxy flavone (quercetin). Fractionation of the acetates yields in the first crop pure quercetin acetate, then mixtures as the intermediate fractions, and in the later fractions kæmpferol acetate. Thus it is clear that

the podophyllum resin contains a mixture of flavonols, quercetin and kæmpferol. The difficulties of earlier workers in isolating pure quercetin was explained by Seshadri and Subramanian[13] as due to the inefficient removal of podophyllotoxin and podophylloresin. It would now appear that the difficulties could also be attributed to the presence of kæmpferol in varying proportions.

EXPERIMENTAL

Preparation of Synthetic Flavonols

Synthetic samples of the flavonols were obtained by dealkylating in the usual way the methyl or ethyl ethers prepared synthetically. The flavonol ether was dissolved in a small quantity of acetic anhydride and excess of hydriodic acid (sp. gr. 1·7, 10 c.c. for 1 g.) added with cooling. The mixture was then refluxed in an oil-bath at 140° for 2 hours, cooled, poured into an excess of a saturated solution of sodium bisulphite and then extracted with ether. The ether extract on evaporation gave a pure yellow crystalline product of the flavonol. To ensure purity this was further crystallised from dilute alcohol and the melting point taken.

The following flavonols were prepared from their methyl or ethyl ethers: Kæmpferol from its tetramethyl ether,[14] fisetin from 7-hydroxy-3: 3′: 4′-trimethoxy flavone,[15] datiscetin from its 3: 2′-dimethyl ether,[16, 17] morin and resomorin both from their 3: 2′: 4′-trimethyl ethers,[17] robinetin from its pentamethyl ether,[18] quercetin from its 3: 3′: 4′-trimethyl ether,[19] myricetin from 3-ethoxy-5: 7: 3′: 4′: 5′-pentamethoxy flavone,[20] quercetagetin from its hexamethyl ether[21] and gossypetin from its 3: 3′: 4′-trimethyl ether.[22]

Flavonols from natural plant sources could also be used in place of synthetic samples, after sufficiently purifying them through the acetate. This was verified in the case of quercetin and gossypetin. The natural flavonols were fully acetylated and the acetate completely purified by crystallisation from ethyl acetate. The fraction having the correct melting point was then hydrolysed using 1 : 1 alcoholic hydrochloric acid, by gently boiling the mixture for 15 minutes. The yellow solution obtained was then diluted with water and extracted with ether. The ether extract on evaporation gave pure yellow crystals of the free flavonol. The purity of the samples was checked by taking their melting points.

Circular (Horizontal Migration) Chromatography : Details and Results

The procedure adopted was essentially the same as that followed by Rao and Beri.[5] Acetone was the solvent chosen to dissolve the flavonol, because of the ease with which it evaporated from the filter-paper, leaving

the pigment spot in the centre. The temperature used was 36–37°. There was no special reason for selecting this temperature, except for the fact that it was the convenient temperature for the double-walled incubator which was used as a thermostat and the room temperature in hot weather at Delhi is not appreciably less. The time of diffusion was only 90 minutes; in this period each flavonol spread itself into a circular zone of convenient size. For preparing a suitable solvent, phenol distilled over zinc dust was shaken up with excess of water and allowed to stand at room temperature (30°), when separation into two layers took place. The lower layer of water in phenol was tapped off and found to be a satisfactory solvent. To obtain correct and reproducible Rf values, certain precautions were necessary. The solvent once prepared was not used for more than a week, since otherwise the zones were not sharp and the Rf values were not consistent. It was also allowed to stand at the temperature of the experiment for at least 48 hours.

The circular Rf values for the important flavonols whose preparation has been given above are listed in the following table:

TABLE I

Flavonol	Rf value (Distance travelled by the solute) / (Distance travalled by the solvent)	Position of hydroxyl groups
1. Kæmpferol ..	0·78	3:5:7:4′
2. Fisetin ..	0·64	3:7:3′:4′
3. Datiscetin ..	0·78	3:5:7:2′
4. Resomorin ..	0·47	3:7:2′:4′
5. Morin ..	0·41	3:5:7:2′:4′
6. Quercetin ..	0·54	3:5:7:3′:4′
7. Robinetin ..	0·44	3:7:3′:4′:5′
8. Myricetin ..	0·30	3:5:7:3′:4′:5′
9. Quercetagetin ..	0·35	3:5:6:7:3′:4′
10. Gossypetin ..	0·28	3:5:7:8:3′:4′

The Rf values given above support in general the conclusions of Batesmith,[23] that the number of hydroxyl groups has an important influence and that the effect of chelatio (especially of the hydroxyl in the 5-position)

brings about an increase in the Rf values. Even other positions are not all equivalent and different arrangements give appreicably different Rf values: *cf.*, numbers 1 to 4, 5 to 7 and 8 to 10, in the table. Thus isomers in many cases seem to be capable of being differentiated by their Rf values. However, it may be mentioned that with this solvent though the compounds can be identified when present alone or with flavonols having less or more number of hydroxyl groups, with mixtures of isomers the rings tend to be broad and separation is not very distinct. Probably other solvents may serve better in these cases.

Extraction of the Plant Materials

Fresh flowers were employed and extracted repeatedly with cold or hot 95% alcohol, the combined extracts concentrated to small bulk and hydrolysed using sulphuric acid (7%). Any alcohol remaining after hydrolysis was removed by evaporation from a porcelain basin, the brownish yellow solution filtered hot, diluted with water and ether extracted. The ether extract on evaporation gave a yellow residue and this was used for chromatography.

Chromatography of Natural Pigments

The flavonol aglycones were chromatographed by the horizontal migration technique and the circular Rf values calculated for the various zones. The sources of the flavonols along with the number of zones and their Rf values are given in the following table:

TABLE II

Source of the flavonol aglycones	Number of zones	Rf_1	Rf_2	Rf_3
Flowers of *Moringa pterygosperma* (both sweet and bitter varieties)	2	..	0·56	0·80
Neem flowers ..	3	0·31	0·54	0·75
Podophyllum emodi (Indian podophyllum) resin	2	..	0·54	0·78

Moringa pterygosperma

Extraction and Isolation of the Colouring Matter

There are two varieties of *M. pterygosperma*, the leaves, flowers and fruits of one variety being bitter while those of the other variety are not. Flowers of both these varieties were extracted and studied separately. 3 kg.

each of the fresh winter flowers were extracted repeatedly in the cold with 95% alcohol, each time the solvent being allowed to stand in contact with the flowers for 2 days. The combined extracts were concentrated to about 200 c.c. by distilling off the excess of alcohol on a boiling water-bath. The concentrate was cooled and allowed to stand for 12 hours, when most of the wax and oil present separated out as a greenish flocculent mass. This was filtered off, through a fluted filter paper, and the precipitate washed with small quantities of 50% alcohol until the test with magnesium and hydrochloric acid was not given. The washings were combined with the original filtrate and the excess of alcohol removed by evaporation in a porcelain basin over a water-bath. The extract which was about 200 c.c. was cooled, and treated with 8 c.c. of concentrated sulphuric acid diluted with 20 c.c. of water, and gently refluxed on a wire-gauze for 2 hours. It was then diluted with twice the volume of water and the whole evaporated in a broad evaporating basin on a water-bath to remove all traces of alcohol. The remaining portion was then filtered hot, the filtrate cooled and extracted repeatedly with ether. The combined ether extracts were washed with water, dried over anhydrous sodium sulphate and distilled to remove solvent. A yellow residue containing some resin was obtained. This was dissolved in the minimum of 50% alcohol, shaken with animal charcoal, heated to boiling and filtered hot. Most of the resins were adsorbed by the animal charcoal and a clear deep yellow filtrate obtained, which on cooling deposited a pure yellow crystalline solid. Yield 0·50 g. from the sweet variety and 0·47 g. from the bitter variety.

In earlier experiments the air-dried flowers were extracted with boiling alcohol, and this involved a number of difficulties. The flowers contain a large quantity of resinous and waxy matter and these were easily extracted by boiling alcohol, and the hot concentrated extract on cooling deposited large quantities of this dark resinous matter, which answered the magnesium-hydrochloric acid test very strongly. Most of the flavonol was thus carried away in the resin and isolation was rather difficult. So in later experiments cold extraction of the fresh flowers was employed as described above, and found to be more convenient since in the cold most of the resin was not extracted. The buds were also used for extraction and the yield of flavonol was found to be the same as in the case of the flowers.

The samples obtained from both the varieties sintered at about 200° and melted over a large range. With magnesium powder and hydrochloric acid a deep red colour was developed in both cases, a colour reaction characteristic of flavonols. With ferric chloride both gave an olive green colour. They did not dissolve in sodium bicarbonate, but with sodium carbonate

they gave a yellow solution. With sodium hydroxide they gave a yellow solution which on shaking with air turned reddish brown. The samples when analysed by the circular paper chromatography, gave 2 rings closely corresponding to kæmpferol and quercetin.

Separation of Methyl Ethers

The flavonol mixture (0·4 g.) was dissolved in pure, dry acetone and treated with excess of pure dry dimethyl sulphate (5 c.c.) and freshly ignited potassium carbonate (5 g.). The mixture was refluxed on a water-bath for 42 hours. Acetone was then distilled off and the residue treated with excess of water, when the methyl ether separated out in the form of an almost colourless solid. This was filtered off, and purified further by crystallising from very dilute alcohol; colourless needles, sintering at 60° and melting at 75–108°, yield 0·27 g.

The methyl ether mixture (0·27 g.) was dissolved in pure dry acetone (20 c.c.) and the solution allowed to pass through a column of activated alumina (Merck) (18 cm. by 1 cm.) under gentle suction. The column was then successively washed with acetone-petroleum ether mixture (1 : 2) using 15 c.c. each time. The fractions were collected separately and the dissolved solid was obtained by evaporating off the solvent and crystallising the residue from the same solvent mixture. Details of analysis are given below:

TABLE III

Serial number	Fraction	Yield in mg.	Melting point
1	Original filtrate	Nil	..
2	Acetone-petroleum ether (1: 2) (15 c.c.)	100	Sintered at 140° and melted at 151–52°
3	do	30	151–52
4	do	50	151–52
5	do	20	151–52
6	do		
7	do		
8	Acetone-petroleum ether (2:2)		

Fractions 3 to 8 were found to be identical with quercetin pentamethyl ether. Fraction 2 was recrystallised from acetone-ligroin mixture. The first crop again had an indefinite melting point (152–62°) whereas the second melted sharp at 151–52° and was identical with quercetin penta-

methyl ether. Further crystallisation of the first crop yielded a small quantity of an ether melting at 162° and it did not depress the melting point of a pure sample of kæmpferol tetramethyl ether (165°). Thus the ether mixture consisted mainly of quercetin along with a small amount of kæmpferol.

Fractionation of the Acetates

The acetate was prepared from the sample obtained from the bitter variety. 0·2 g. of the flavonol was dissolved in excess of acetic anhydride (3 c.c.) and freshly fused sodium acetate (0·5 g.) added. The mixture was refluxed on an oil-bath at 138–40° for 2 hours and poured on to crushed ice with constant stirring. The acetate soon separated out as a colourless solid, partly in the form of needles. Yield 0·23 g. It crystallised from absolute ethyl acetate as colourless needles, m.p. 172–78°.

The acetate mixture was dissolved in a liberal volume of hot absolute ethyl acetate and allowed to stand for 12 hours. The first fraction that separated out was filtered off, and was found to melt at 190–91°. The mixed melting point with an authentic sample of quercetin penta-acetate was undepressed. Subsequent fractions also melted at 190°, and the last fraction at 181–84°. The yield of the last fraction was only 30 mg. Mixed melting point of this fraction with pure quercetin penta-acetate was 181–90°. Since no considerable depression in the melting point was shown, it was concluded that the quercetin acetate which formed the main fraction in the acetate mixture was contaminated with a trace of an unisolatable impurity. This impurity may be the acetate of kæmpferol as indicated by paper chromatography.

Separation through the Glycosides

Neutral lead salt fraction (*Quercetin*).—1 kg. of the fresh flowers (bitter variety) were extracted in the cold with 95% alcohol, twice repeatedly. The extracts were combined and the excess of alcohol distilled off on a boiling water-bath, and the concentrated solution cooled, when plenty of chlorophyll and waxy matter separated out. This was filtered off, and the filtrate treated with an excess of a concentrated solution of neutral lead acetate. The lead salt of quercetin glycoside separated out as a bulky yellow precipitate. This was filtered off (filtrate marked F), washed well with water, suspended in alcohol, and a current of hydrogen sulphide passed through for 2 hours, till all the lead was removed in the form of lead sulphide. The black precipitate of lead sulphide was filtered off. This was then ground in a mortar with a small quantity of alcohol to remove traces of the glycoside present along with it, and filtered. The filtrate was combined with the

original filtrate and hydrogen sulphide again passed through. No appreciable precipitation of lead sulphide took place, indicating the complete removal of lead from the lead salt. The alcoholic filtrate containing the glycoside in solution was concentrated. It gave a positive test with zinc and concentrated hydrochloric acid (Pew's reaction)[7] thereby indicating that the sugar molecule is attached to the 3-position. At first a faint orange yellow colour developed which gradually became more and more intense on keeping and assumed a deep orange red colour after 2 days. The yellow colour of the lead salt also indicated the presence of a 3-glycoside.

The concentrated alcoholic solution was subjected to acid hydrolysis in the usual way, and the aglycone extracted with ether, and the ether distilled off, when a yellow residue was obtained (0·25 g.). This gave a deep red colour with magnesium and hydrochloric acid. With zinc and hydrochloric acid no colour was developed, showing that the 3-hydroxyl was free.

The yellow residue when analysed by paper chromatography gave a single yellow zone, having an average Rf value of 0·55 which corresponded with that obtained for pure synthetic quercetin. The identity was confirmed by preparing the acetate and taking the mixed melting point with an authentic sample of quercetin penta-acetate. Yield 0·12 g.

Basic lead salt fraction (*Kæmpferol*).—The filtrate (F) left behind after removal of the neutral lead acetate precipitate was treated with a large excess of basic lead acetate. A lemon yellow flocculent precipitate was obtained. This was filtered off, suspended in alcohol and decomposed with hydrogen sulphide. The alcoholic solution of the glycoside (which gave a positive test for Pew's reaction) was hydrolysed as usual; the aglycone was found to be kæmpferol by means of the acetate which lost water at 118° and melted at 180–85°.

In the above experiments using the separation of the glycosides, it was possible to obtain both the quercetin and the kæmpferol fraction more definitely. This may be attributed not only to the improved technique but also to the effect of seasonal variations on the pigment composition. Kæmpferol seems to be present more in the later flowers.

The aqueous acid solutions left after ether extraction of the flavonol aglycones were separately treated with barium carbonate little by little, till all the sulphuric acid was removed as barium sulphate and the solutions became neutral to litmus. The insoluble barium sulphate was filtered off and the filtrates containing the sugar concentrated to convenient bulk. Both yielded the same osazone which was identified as glucosazone.

Neem Flowers

Isolation of the Colouring Matter

Neutral lead salt fraction (*Quercetin and myricetin*).—200 g. of the air-dried flowers were soaked with water and allowed to stand for 12 hours. Alcohol was then added and the flowers repeatedly extracted thrice, each time refluxing on a water-bath for 6 hours. The combined extracts were concentrated and treated with an excess of neutral lead acetate. The bulky yellow precipitate of the neutral lead salt was filtered off (filtrate marked A), suspended in aqueous alcohol and decomposed by passing hydrogen sulphide. Lead sulphide was filtered off and the glycoside remaining in the filtrate was hydrolysed using sulphuric acid (7%). Alcohol was removed by evaporation from a basin. On cooling a yellow amorphous mass separated out. This was extracted with ether and the ether extract evaporated when a yellow residue was obtained which when analysed by paper chromatography gave two distinct zones corresponding to myricetin and quercetin. It was crystallised from 50% alcohol and pure yellow crystals obtained. Yield 0·42 g. The product gave with aqueous sodium carbonate and sodium hydroxide an emerald green colour which on shaking quickly changed into a purplish violet. This indicated the presence of myricetin in the crystalline product.

0·4 g. of the above product was acetylated using acetic anhydride and pyridine. The acetate mixture came out as colourless needles from ethyl acetate; yield 0·5 g., sintering at 108° and melting between 140–68°. The fractionation of the acetate was done using ethyl acetate as solvent. The first crop of crystals (100 mg.) sintered at 200° and melted at 204°. Recrystallisation of this from the same solvent yielded colourless crystals melting at 212–14°. The mixed melting point with an authentic sample of myricetin hexa-acetate was undepressed. The intermediate fractions did not melt sharp and the later fractions melted correctly at 191–92°, and were identical with quercetin acetate. The mixed melting point with an authentic sample of quercetin acetate was not lowered.

Basic lead salt fraction (*Kæmpferol*).—The filtrate (A) obtained from the neutral lead salt was treated with an excess of basic lead acetate, when a lemon yellow precipitate was formed. This was filtered off, deleaded and the alcoholic solution containing the glycoside hydrolysed using sulphuric acid (7%). Excess alcohol was then removed by evaporation from a porcelain basin and the aglycone extracted with ether. The ether extract on distillation left behind a yellow crystalline solid. This was further purified by crystallising from dilute alcohol. Yield 0·4 g., m.p. 276–78°. It

agreed with pure kæmpferol and the mixed melting point with an authentic sample of kæmpferol was undepressed.

The proportions of the three pigments in the flowers were approximately as follows: Myricetin 3, quercetin 7 and kæmpferol 10 parts.

The Glycosides

The yellow colour of the lead salts indicated that all the three flavonols might be existing as their 3-glycosides. This was further supported by the positive Pew's reaction,[7] given by each of the fractions.

Indian Podophyllum (*Podophyllum emodi*)

Podophyllum resin was supplied by the Drug Research Laboratories, Jammu-Tawi. For the isolation of the colouring matter from this, 40 g. of the resin was taken up in acetone (100 c.c.) and filtered. The filtered solution was then treated with chloroform (800 c.c.) and shaken vigorously. The clear solution was decanted off from the sticky resin that was precipitated and diluted with an equal volume of chloroform. The crude colouring matter separated out as a fine yellow powder (1 g.). This was filtered off and crystallised from dilute alcohol. Yellow crystals, yield 0·8 g.

Fractionation of the Acetate

0·8 g. of the flavonol mixture was converted into the acetate using acetic anhydride and pyridine. Yield, quantitative. The fractionation of the acetate was done using ethyl acetate as solvent. The first crop of crystals melted at 192–93°, corresponding to quercetin acetate. The subsequent fractions did not melt sharply; later fractions sintered at 120° and melted at 140°. These when recrystallised lost water at 120° and melted at 185°. Tail fractions also behaved similarly and were found to be identical with kæmpferol acetate. The mixed melting point with a genuine sample of kæmpferol tetra-acetate was undepressed. Yield, 0·15 g. The proportions of quercetin and kæmpferol were approximately 87% and 13% respectively.

Another sample of *Podophyllum emodi* supplied by Stafford Allen & Sons Ltd., London, was also examined for the colouring matter; 40 g. of the resin gave 2·3 g. of the almost pure colouring matter, the yield being thus thrice that obtained from the Jammu-Tawi sample. Paper chromatography indicated the presence of two flavonols corresponding to quercetin and kæmpferol. Separation of these two was effected through the fractionation of the acetate mixture, and the proportions of quercetin and kæmpferol were found to be roughly 80% and 20% respectively.

Summary

Circular Rf values of important synthetic flavonols have been determined using phenol saturated with water. The results have been used for analysing the flavonol composition of plant extracts, three typical examples being taken; *Moringa pterygosperma* flowers, Neem flowers and Indian Podophyllum (*Podophyllum emodi*) resin. The results have been verified by applying regular methods of fractionation involving lead salt precipitation, fractional crystallisation of the acetates and adsorption chromatography of the methyl ethers. These materials could therefore be used as standards of comparison where synthetic flavonols are not readily available. Some information about the nature of the glycosides have been provided by colour reactions.

Our thanks are due to Mr. S. Varadarajan of this Department for the help he has rendered in the isolation of the colouring matter of the Neem flowers and *Podophyllum emodi* resin (Jammu-Tawi).

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STUDIES IN ELECTRETS—PART I

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1. Introduction

Though a large amount of work has been done on magnets and magnetic material, the electrical counterpart, 'the electret' and the material suitable for its preparation have not yet attracted the attention they deserve. The properties of the electret are remarkable, whether one looks at them in the light of the classical theory or the modern theory of semi-conductors and insulators. The effects associated with the formation of the electret are peculiar in many respects and add further to the abnormal properties of dielectrics.

The name 'electret' was first proposed by Heaviside, in analogy to the magnet, for a body permanently charged with electricity. However, the first electret was prepared by Eguchi[1] from mixtures of certain natural waxes and resins in equal proportions and also a little of beeswax. He allowed the molten mixture to solidify under a high electric field and on removing the field, found the solid to have acquired electric charges of opposite signs at the two surfaces where electric field was applied. After allowing for settling time, these charges attain steady values and retain their strength apparently indefinitely if properly kept.

There is a close similarity between the properties of an electret and those of a magnet, though there are certain characteristic differences too. The electrification of an electret is a volume effect and not a surface effect, as is observed in electro-statics in frictional electricity. The electret cut transverse to the axis—the line joining the poles—retains its electrical properties in either of its parts, just as a magnet. Further an electret requires 'keepers' to maintain its charge, like a magnet. Melting destroys the electrification permanently, while exposure to moist air or ultra-violet light or X-rays, destroys it temporarily only; the original charge can be reestablished in its full strength by restoring the original conditions. When freshly prepared, all electrets exhibit polarity opposite in sign to that of the adjoining

electrode of the field; this charge is called as 'heterocharge' by Gemant.[2] After the electric field applied during formation of an electret is removed, these heterocharges generated show a decrease in the initial stages in all cases. In some cases however, the charges acquire a permanent value after some time, while in other cases they show a reversal of charges, and each pole acquires the same polarity as that of the adjoining electrode during formation; these charges are called 'homo-charges'. To these peculiar properties a few more additions can be made, *e.g.*, the hysterisis effect, piezo-electric effect, etc. But a good many of these observations lack confirmation and detailed investigations.[3] Dielectrics are well known for their abnormal behaviour under certain conditions and hence it is highly essential to study systematically each aspect of the electret during its formation under carefully controlled conditions. The simplest to study will be to observe the change in the steady current flowing through the electret composition during its formation by changing the electric field and also the temperature.

2. Apparatus and Method

Most of the workers in this field have followed Eguchi and used mixtures of waxes to prepare electrets[4] or the constituents of the waxes[2] and other organic solids. Later workers tried a few inorganic solids too.[5] However, Carnauba wax seems to be the principle ingredient used most generally. The other ingradients are added mostly to increase the mechanical strength and elasticity of the electret so that it can be turned to any desired shape and size. Carnauba wax alone therefore was chosen for this preliminary investigations. The wax was purchased from the market and was a May and Baker product.

Carnauba wax was taken in a small pyrex beaker and this beaker was kept in a large size beaker containing oil. Two thick pieces of copper (size 3×3 cm.) covered with tin foil were introduced in the wax when in molten state. Each of these two pieces of copper was fixed to a stout copper rod. These electrodes were kept at a fixed distance in a framework of ebonite. This distance could be altered to any desired value, but in the following experiments it was kept about 5 mm.

Best electrets are formed with electric fields of the order of 10 kilovolts per cm. Electrification does occur with even lower fields, but the characteristics of electrets formed with lower fields are somewhat different. In the present investigations the higher fields were taken from a high voltage D.C. source giving voltages upto 5 Kilovolts in steps of 1 kilovolt. For lower fields the usual high tension batteries were used. The primary of the high voltage D.C. source was fed through a constant voltage transformer.

The steady current through the wax was measured by a sensitive suspension galvanometer, with or without shunt as was necessary.

The outer beaker was heated from below and the oil was continuously stirred by a stirrer to keep the temperature round the inner beaker uniform. The temperature of the wax between the electrodes was measured by a thermometer kept in it. Electric field was applied when the wax was in a liquid state and the heat was withdrawn. The cooling of the inner beaker was rather slow due to the presence of the outer beaker. Slow cooling is necessary for the molecules of carnauba wax to get properly oriented and fixed. Whenever rapid cooling was required the outer beaker was removed.

Carnauba wax is a product of the palm species *Copernicia* (or *Copernica*) *cerifera*, obtained from the exudations of the leaves and peticoles.[6] It is not a definite chemical compound but a mixture of different organic substances. Various methods are followed by different firms for its extraction and refining. It was therefore necessary to investigate first the suitability of the sample for the preparation of electrets. Some of the experiments of the previous workers, particularly of Gemant, Mikola and Adams,[7] were repeated. The portion of the wax between the electrodes was removed and cut to shape and size as required. It showed all the characteristics observed by previous workers. The sample of carnauba wax therefore was suitable for studies in electrets.

3. STEADY CURRENT AND THE 'HYSTERESIS' EFFECT

Carnauba wax is a poor conductor of electricity, though not as poor as paraffin and beeswax; hence the steady currents can be measured without much difficulty under various conditions. The outer beaker was heated and a known voltage was applied to the electrodes. The steady current was measured at various temperatures as indicated by the thermometer. Currents were measured when the wax was in the solid state as well as when it was in the liquid state, upto about 90° C. when the wax is in a thoroughly molten state. In the preparation of electrets there is little advantage in exceeding this temperature.[8] Readings were taken for a fixed voltage while cooling the wax as well as while heating the wax. While cooling the electret is being formed, whereas it is being destroyed while being heated to melt.

When in the liquid state, the wax shows a high conductivity as is to be expected. As the temperature is lowered the current flowing through the wax decreased linearly with temperature. At about 83° C. a sharp break in the linear relationship was observed and the current decreased much more rapidly with decrease in temperature. At about 75° C. the decrease became less rapid and within a range of about 5° C. the current became negligible.

For temperatures below 70° C. the current could hardly be measured accurately with a suspension galvanometer. When the wax had attained room temperature, the outer beaker was again heated and similar readings were taken with temperature rising. In these sets of experiments the current was negligible upto about 80° C. or thereabouts and then increased, first slowly and then rapidly.

Current passing through the wax was measured in this way by applying a steady voltage which was varied from a few volts to 5 kilovolts. For all these values of electric field the nature of the curve was substantially the same. However, it was observed that for all values of the impressed voltage at any particular temperature, the current observed while heating was different from that observed while cooling and hence the curves obtained by plotting the current against temperature showed a loop similar to that usually observed in B–H curves. This ' Hysteresis ' effect has been reported in the case of paraffin wax alone.[9] During cooling, all the curves show a sharp break at about 83° C.—the melting point of carnauba wax. While during heating no such break at 83° C. was observed; the current increased slowly from about 80° C. and near about 90° C. the rise became very sharp the curves becoming nearly vertical.

To verify whether this ' Hysteresis ' effect is genuine or spurious, due to the lack of thermal equilibrium in the wax by virtue of the poor thermal conductivity of carnauba wax, the rate of heating and also of cooling was decreased. The width of the ' Hysteresis ' loop was observed to be a function of the rate of heating and cooling. By making the rate so slow as to allow the entire wax to attain uniform temperature, the hysteresis loop totally disappeared, proving that the hysterisis effect in the case of carnauba wax is spurious. Further experiments were performed to test this conclusion by changing the geometry of the apparatus and in every case where the rate of cooling and heating was very slow, the two curves coincided and the loop disappeared. The hysteresis effect is therefore entirely due to the lack of thermal equilibrium.

Besides the absence of hysteresis effect in steady currents, certain other interesting facts emerge out of these investigations. The steady current shows a gradual rise at 73° C., but from 75° C. the rise is very rapid. The wax has thus become soft in this region of temperature but not melted. It is in this condition we can expect the electret to be formed if the electric field is applied. It is of little use to apply the field at lower or higher temperatures. This agrees very closely with the observations of the previous workers.[3] The molecules in the wax become mobile above this temperature and hence

cannot take proper orientation. At temperatures between 80° C. and 83° C the wax is completely in a liquid condition as shown by the sharp break in the curve. The rate of change of steady current in the liquid state is observed to be less than that in the soft state. Secondly, if the straight portion of the curve starting from the melting point is produced further to cut the temperature axis, this sharp—practically vertical—rise in the curve is observed to remain within 2° to 3° C. in all curves. The rounded portion of the steady current *vs.* temperature curves appears to be important in understanding the peculiarities observed with electrets prepared from carnauba wax.

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SUMMARY

The steady current characteristics of carnauba wax are studied with the view to understanding the mechanism of formation and properties of electrets. Careful investigations show that the 'hysteresis effect' is totally absent in steady currents observed while cooling and heating carbaube wax under the influence of electric field. The electric field was varied from a few volts per cm. to 10 kV per cm. The rate of change of current with temperature is very small below 75° C. for all voltages and increases very rapidly for higher temperatures upto the melting points. Beyond the melting point the rate again falls.

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THE SECOND CURVATURE OF A GEODESIC ON A HYPERSURFACE OF A RIEMANNIAN SPACE

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Introduction

The object of this paper is to find expressions for the first torsion of a geodesic of a hypersurface of a Riemannian space and to find the directions for which the torsion of the geodesic is a maximum or a minimum. The expressions (5) and (8) are generalizations of the corresponding results in differential geometry of a surface in Euclidean 3-space. We also deduce some interesting corollaries. Formula (12) provides a sort of approximation to Enneper's formula relating to the torsion of an asymptotic line in ordinary differential geometry. Theorem 2 is also an interesting generalization.

1. A curve in a Riemannian space V_n of n dimensions has $(n-1)$ mutually orthogonal and independent normals and $(n-1)$ curvatures defined by the following equations which are generalizations of the Serret-Frenet formulæ of the three-dimensional differential geometry[1]:

$$\frac{\delta \mathbf{b}_{r/}{}^{i}}{\delta s} = \mathbf{b}_{r+1/}{}^{i}\, c_{r+1} - \mathbf{b}_{r-1/}{}^{i}\, c_r, \tag{1}$$

where we call $\mathbf{b}_{r/}{}^{i}$ as the components of the $(r-1)$th binormal and c_r, *the rth curvature*. $\mathbf{b}_{0/}{}^{i}$ is the unit tangent vector $\mathbf{t}^i$ to the curve and $c_0 = c_n = 0$. The tangent and the $(n-1)$ normals at a point form n mutually orthogonal vectors.

A curve which lies in a hypersurface V_n of an $(n+1)$-dimensional Riemannian space V_{n+1}, can also be considered as a curve in V_{n+1} and as such has n curvatures and n mutually orthogonal normals in V_{n+1}. The geodesic tangent in V_n to the curve has n orthogonal normals and n curvatures in V_{n+1}. We shall adopt the following symbols to represent these quantities.

1. C .. A curve in V_n.
2. T^α, t^i .. Components in V_{n+1} and in V_n respectively of the unit tangent to C.
3. $B_{r/}{}^\alpha$, $b_{r/}{}^i$ $(r = 1, \ldots . n-1)$ Components in V_{n+1} and in V_n of the unit principal normal and binormals in V_n to C.
4. $\xi_{r/}{}^\alpha$, $(r = 1, \ldots . n)$ .. Unit principal normal and $(n-1)$ binormals in V_{n+1} to C.
5. $c_1, \ldots . c_{n-1}$ .. The $(n-1)$ curvatures in V_n of C.
6. $K_1, \ldots . , K_n$ .. The n curvatures in V_{n+1} of C.
7. s .. Arc of C.
8. $\frac{\delta}{\delta s}$ .. Intrinsic derivative operator along T^α.
9. G .. Geodesic tangent in V_n to C at a point P.
10. S .. Arc of G.
11. $\frac{\delta}{\delta S}$ .. Intrinsic derivative operator along G.
12. N^α, $N_{r/}{}^\alpha$, $(r=1, \ldots . , n-1)$ Unit principal normal and $(n-1)$ binormals in V_{n+1} to G.
13. $n_{r/}{}^i$ $(r = 1, 2, \ldots . , n-1)$ Components in V_n of $N_{r/}{}^\alpha$, $(r = 1, \ldots . , n-1)$.
14. $\tau_1, \ldots . , \tau_n$ .. The n curvatures in V_{n+1} of G.
15. $\frac{1}{\rho_1}, \ldots . , \frac{1}{\rho_n}$ .. The principal curvatures of V_n in V_{n+1}.
16. $e_{p/}{}^i$, $(p = 1, \ldots . , n)$ .. Unit vectors along principal directions of V_n.
17. $E_{p/}{}^\alpha$, $(p = 1, \ldots . , n)$ .. Components in V_{n+1} of $e_{p/}{}^i$, $(p = 1, \ldots . , n)$.

Throughout Greek indices run through the values $1, 2, \ldots . , n+1$, while Latin indices run through $1, \ldots . , n$.

We note here that N^α, the principal normal to G is the normal to V_n. τ_1, the first curvature of G is the normal curvature of V_n along t^i. $N_{r/}{}^\alpha$, $(r = 1, \ldots . , n-1)$ are tangential to V_n.

The second of the Serret-Frenet formulæ applied to G in V_{n+1} at P gives

$$\frac{\delta N^\alpha}{\delta s} = \frac{\delta N^\alpha}{\delta S} = \tau_2 N_{1/}{}^\alpha - \tau_1 T^\alpha, \qquad (2)$$

and squarnig both sides,

$$\left(\frac{\delta \mathbf{N}}{\delta s}\right)^2 = {\tau_1}^2 + {\tau_2}^2,$$

which correspond to the formulæ

$$\left.\begin{aligned} \frac{d\mathbf{N}}{ds} &= \tau_g \vec{\mathbf{b}} - k_n \vec{\mathbf{t}} \\ \text{and} \qquad \left(\frac{d\mathbf{N}}{ds}\right)^2 &= {\tau_g}^2 + {k_n}^2 \end{aligned}\right\},$$

for a curve on a surface in ordinary space.

Next we have[1]

$$-\tau_2 = -\mathbf{N}_{1/} \cdot \frac{\delta \mathbf{N}}{d\mathbf{S}} = \mathbf{N} \cdot \frac{\delta \mathbf{N}_{1/}}{d\mathbf{S}} = \mathbf{N} \cdot \left[(\Omega_{ij} \mathbf{n}_{1/}{}^i \mathbf{t}^j)\, \mathbf{N} + \frac{\delta \mathbf{n}_{1/}{}^i}{d\mathbf{S}}\, y_{,i} \right], \qquad (3)$$

where $\frac{\delta \mathbf{n}_{1/}{}^i}{ds}$ is the intrinsic derivative in V_n of $\mathbf{n}_{1/}{}^i$ which is therefore tangential to V_n, and Ω_{ij} is the second fundamental tensor of V_n. $\mathbf{P}.\mathbf{Q}$ means the "scalar product" $a_{\alpha\beta}\mathbf{P}^\alpha \mathbf{Q}^\beta$, $a_{\alpha\beta}$ being the fundamental tensor of V_{n+1}. A similar meaning will be given to scalar product in V_n.

Therefore
$$\tau_2 = -\Omega_{ij} \mathbf{n}_{1/}{}^i \mathbf{t}^j. \qquad (4)$$

This is the simplest expression for the *second curvature* or the *first torsion* in V_{n+1} of G.

Next we can express $\mathbf{t}^i$ as

$$\mathbf{t}^i = \sum_{p=1}^{n} \mathbf{e}_{p/}{}^i \cos\theta_p,$$

where θ_p is the angle between $\mathbf{e}_{p/}$ and $\mathbf{t}$. From (2),

$${\tau_1}^2 + {\tau_2}^2 = \left(\frac{\delta \mathbf{N}}{\delta \mathbf{S}}\right)^2 = (\mathbf{N}_{;i}\, \mathbf{t}^i)^2$$

$$= \left[\sum_{p=1}^{n} \mathbf{N}_{;i}\, \mathbf{e}_{p/}{}^i \cos\theta_p \right]^2 = \left[-\sum_{p=1}^{n} \frac{\mathbf{E}_p}{\rho_p} \cos\theta_p \right]^2,$$

on account of the property that the intrinsic derivative of unit normal along a principal direction is co-directional with the latter.[3] Thus

$${\tau_1}^2 + {\tau_2}^2 = \sum_{p=1}^{n} \frac{\cos^2\theta_p}{{\rho_p}^2}.$$

$$\therefore \qquad {\tau_2}^2 = \sum_{p=1}^{n} \frac{\cos^2\theta_p}{{\rho_p}^2} - {\tau_1}^2$$

$$= \sum_{p=1}^{n} \frac{\cos^2\theta_p}{{\rho_p}^2} - \left[\sum_{p=1}^{n} \frac{\cos^2\theta_p}{\rho_p} \right]^2,$$

using Euler's theorem,[4] so that

$$\tau_2{}^2 = \sum_{p=1}^{n} \frac{1}{\rho_p{}^2} \cos^2\theta_p (\cos^2\theta_1 + \ldots + \cos^2\theta_n) - \sum_{p=1}^{n}\sum_{q=1}^{n} \frac{\cos^2\theta_p}{\rho_p} \frac{\cos^2\theta_q}{\rho_q}.$$

Thus
$$\tau_2{}^2 = \frac{1}{2}\sum_{p=1}^{n}\sum_{q=1}^{n} \cos^2\theta_p \cos^2\theta_q \left(\frac{1}{\rho_p} - \frac{1}{\rho_q}\right)^2 \tag{5}$$

which is to be considered as the extension of the well-known result

$$\tau_g = \sin\theta\cos\theta\left(\frac{1}{\alpha} - \frac{1}{\beta}\right)$$

of three-dimensional differential geometry.

From (5) we deduce that, for a general point, τ_2 is zero only for a principal direction. [This is seen from (2) also since the intrinsic derivative of the unit normal along a principal direction is co-directional with the latter] and $\tau_2 = 0$ for all directions at an umbilic.

Also $\tau_2{}^2$ *is the same for all directions given by*

$$\mathbf{a}^i = \sum_{p=1}^{n} \pm \cos\theta_p \mathbf{e}_p{}^i,$$

for different combinations of the positive and negative signs.

3. MAXIMA AND MINIMA of τ_2

We see from equation (5) that at a point on V_n $\tau_2{}^2$ is a function of $(\cos\theta_1, \ldots, \cos\theta_n)$ which are connected by a single relation $\Sigma\cos^2\theta_p = 1$. Therefore we can treat $(\theta_2, \ldots, \theta_n)$ as independent variables and θ_1 as a function of $(\theta_2, \ldots, \theta_n)$

$$\cos^2\theta_1 = 1 - \sum_{p=2}^{n}\cos^2\theta_p.$$

$$\frac{\partial\theta_1}{\partial\theta_p} = -\frac{\cos\theta_p \sin\theta_p}{\cos\theta_1 \sin\theta_1}.$$

Let us now fix p.

$$\begin{aligned}
\frac{\partial\tau_2{}^2}{\partial\theta_p} &= -\tfrac{1}{2}\sum_{h=1}^{n} 2\cos\theta_p \sin\theta_p \cos^2\theta_h \left(\frac{1}{\rho_p} - \frac{1}{\rho_h}\right)^2 \\
&\quad + \tfrac{1}{2}\sum_{h=2}^{n} 2\cos\theta_1 \sin\theta_1 \cos^2\theta_h \left(\frac{1}{\rho_1} - \frac{1}{\rho_h}\right)^2 \frac{\partial\theta_1}{\partial\theta_p} \\
&= -\sum_{h=1}^{n}\left[\cos\theta_p \sin\theta_p \cos^2\theta_h \left\{\left(\frac{1}{\rho_p} - \frac{1}{\rho_h}\right)^2 - \left(\frac{1}{\rho_1} - \frac{1}{\rho_h}\right)^2\right\}\right] \\
&= -\cos\theta_p \sin\theta_p \left[\sum_{h=1}^{n}\frac{\cos^2\theta_h}{\rho_p{}^2} - 2\sum_{h=1}^{n}\frac{\cos^2\theta_h}{\rho_p\rho_h} - \sum_{h=1}^{n}\frac{\cos^2\theta_h}{\rho_1{}^2}\right. \\
&\qquad\qquad \left. + \sum_{h=1}^{n}\frac{2\cos^2\theta_h}{\rho_1\rho_h}\right] \\
&= -\cos\theta_p \sin\theta_p \left\{\frac{1}{\rho_p{}^2} - \frac{2}{\rho_p}\tau_1 - \frac{1}{\rho_1{}^2} + \frac{2}{\rho_1}\tau_1\right\}.
\end{aligned}$$

Therefore

$$\frac{\partial \tau_2^{\,2}}{\partial \theta_p} = \cos\theta_p \sin\theta_p \left(\frac{1}{\rho_1} - \frac{1}{\rho_p}\right)\left(\frac{1}{\rho_1} + \frac{1}{\rho_p} - 2\tau_1\right). \tag{6}$$

Since $\tau_2 = 0$ only for a principal direction, $\frac{\partial \tau_2}{\partial \theta_p} = 0$ if $\frac{\partial \tau_2^{\,2}}{\partial \theta_p} = 0$, for directions other than principal directions.

For a maximum or minimum of τ_2, $\frac{\partial \tau_2}{\partial \theta_p}$ must vanish for $p = 2, \ldots, n$.

Consider the roots of $\frac{\partial \tau_2^{\,2}}{\partial \theta_p} = 0$.

$$\frac{\partial \tau_2^{\,2}}{\partial \theta_p} = \cos\theta_p \sin\theta_p \left(\frac{1}{\rho_1} - \frac{1}{\rho_p}\right)\left(\frac{1}{\rho_1} + \frac{1}{\rho_p} - 2\tau_1\right)$$

$= 0$ if (i) $\sin\theta_p = 0$

or (ii) $\cos\theta_p = 0$

or (iii) $\frac{1}{\rho_1} = \frac{1}{\rho_p}$

or (iv) $\frac{1}{\rho_1} + \frac{1}{\rho_p} - 2\tau_1 = 0.$

(*a*) $\sin\theta_p = 0$ gives a principal direction in which case $\tau_2 = 0$.

(*b*) Now let all the curvatures be unequal. Then condition (iii) cannot be satisfied for any value of p, and condition (iv) can be satisfied only for one value of p since, otherwise, it leads to $\frac{1}{\rho_p} = \frac{1}{\rho_q}$ against hypothesis. Therefore for al other values of p from 2 to n, condition (ii) must hold, *i.e.*, $\cos\theta_p = 0$. Let (v) be satisfied for the index p and (ii) for all others. Then

$$\frac{1}{2}\left(\frac{1}{\rho_1} + \frac{1}{\rho_p}\right) = \tau_1 = \frac{\cos^2\theta_1}{\rho_1} + \frac{\cos^2\theta_p}{\rho_p},$$

and

$$\cos^2\theta_1 + \cos^2\theta_p = 1$$

which leads to $\cos^2\theta_1 = \cos^2\theta_p = \frac{1}{2} = \cos^2\frac{\pi}{4}$.

Thus $\mathbf{t}^i$ *is equally inclined to* $\mathbf{e}_1{}^i$ *and* $\mathbf{e}_p{}^i$ *and orthogonal to the remaining principal directions.*

(*c*) We next consider the case where there are sets of equal values of curvatures at the point. Let $\rho_1 = \rho_2 = \ldots = \rho_r$, $\rho_1 = \rho_{s+1} = \rho_{s+2} = \ldots = \rho_{s+q}$, etc. Condition (iii) is satisfied for $p = 2, \ldots, r$, $(r, s < n)$. If condition (iv) is not satisfied for any value of p, condition (ii) must hold for all other values of p, *i.e.*, $\cos\theta_p = 0$, $p = r+1, \ldots, n$, in which case $\mathbf{t}^i$,

being orthogonal to $(\mathbf{e}_{r+1}^{i}, \ldots, \mathbf{e}_{n}^{i})$ is a linear combination of $\mathbf{e}_1^{i}, \ldots, \mathbf{e}_r^{i}$, which will again be a principal direction since $\rho_1 = \ldots = \rho_r$.

(*d*) If condition (iii) is satisfied for $p = 2, \ldots, r$ and (iv) holds for one or more values of p, say, $p = s$, then it holds also for $p = s+1, \ldots, s+q$ if and only if $\rho_s = \rho_{s+1} = \ldots = \rho_{s+q}$, and for no other value of p. Therefore for the remaining $(n - r - q - 2)$ values of p, $\cos\theta_p = 0$. In this case condition (iv) becomes

$$\frac{1}{\rho_1} + \frac{1}{\rho_s} = 2\tau_1 = \sum_{p=1}^{n} \frac{\cos^2\theta_p}{\rho_p}$$

$$= \frac{\cos^2\theta_1 + \ldots + \cos^2\theta_r}{\rho_1} + \frac{\cos^2\theta_s + \ldots + \cos^2\theta_{s+q}}{\rho_s}$$

and $\cos^2\theta_1 + \ldots + \cos^2\theta_r + \cos^2\theta_s + \ldots + \cos^2\theta_{s+q} = 1$

which as before leads to

$$\cos^2\theta_1 + \ldots + \cos^2\theta_r = \cos^2\theta_s + \cos^2\theta_{s+1} \ldots + \cos^2\theta_{s+q} = \tfrac{1}{2}.$$

i.e., $\mathbf{t} \cdot \sum_{p=1}^{r} \cos\theta_p \mathbf{e}_{p'} = \left(\sum_{p=1}^{n} \cos\theta_p \mathbf{e}_{p'}\right) \cdot \sum_{p=1}^{r} \cos\theta_p \mathbf{e}_{p'} = \sum_{p=1}^{r} \cos^2\theta_p = \tfrac{1}{2}$

and $\mathbf{t} \cdot \sum_{p=0}^{q} \cos\theta_{s+p} \mathbf{e}_{s+p'} = \sum_{p=0}^{q} \cos^2\theta_{s+p} = \tfrac{1}{2}$.

Thus $\sum_{p=1}^{r} \cos\theta_p \mathbf{e}_{p'}{}^{i}$ and $\sum_{p=0}^{q} \cos\theta_{s+p} \mathbf{e}_{s+p'}{}^{i}$ being each a linear combinaion of principal directions corresponding to equal values of curvature, are themselves principal directions corresponding to distinct values of curvatures. *Therefore* $\mathbf{t}^{i}$ *is a linear combination of any two of the principal direcions corresponding to two distinct values of curvatures and is equally inclind to each of these.*

In cases (*b*) and (*d*), from (5), $\tau_2{}^2$ takes the form

$$\tau_2{}^2 = \tfrac{1}{2} \sum_{p=r,s} \sum_{q=r,s} \cos^2\theta_p \cos^2\theta_q \left(\frac{1}{\rho_p} - \frac{1}{\rho_q}\right)^2$$

$$= \tfrac{1}{2} \cdot \tfrac{1}{2} \left(\frac{1}{\rho_r} - \frac{1}{\rho_s}\right)^2$$

$$\therefore \quad \tau_2 = \pm \tfrac{1}{2} \left(\frac{1}{\rho_r} - \frac{1}{\rho_s}\right)$$

The results of (*a*), (*b*), (*c*) and (*d*) together can be stated as:

THEOREM 1.—*The necessary and sufficient condition that th second curvature of a geodesic be a maximum or a minimum at a point on a hypersurface, is that its tangent vector at the point should be a linear cnbination of two of the principal directions corresponding to any two distin values of*

principal curvatures and that it should be equally inclined to each of these directions. The magnitude of the second curvature in this case is half the difference between the corresponding two principal curvatures.

Further, if the lines of curvature of a V_n in V_{n+1} are indeterminate the second curvature of any geodesic is zero and conversely.

For, if the lines of curvature are indeterminate, $\Omega_{ij}=\lambda g_{ij}$ where Ω_{ij} and g_{ij} are second and first fundamental tensors of V_n respectively and λ is a constant.

Therefore $\tau_2 = -\Omega_{ij}\,\mathbf{n}_{1/}{}^{i}\mathbf{t}^{j} = -\lambda g_{ij}\,\mathbf{n}_{1/}{}^{i}\mathbf{t}^{j} = 0.$

Since $\mathbf{n}_{1/}{}^{i}$ and $\mathbf{t}^{i}$ are orthogonal.

Conversely, if $\tau_2 = 0$, for all directions, by (4), the point is an umbilic, *i.e.*, the lines of curvature are indeterminate.

4. Let $\mathbf{v}^{i}$ and $\mathbf{V}^{\alpha}$ be the components in V_n and V_{n+1} of a unit vector in V_n. We know that[5]

$$-\Omega_{ij}\mathbf{t}^{i}\mathbf{v}^{j} = \frac{\delta \mathbf{N}}{\delta \mathbf{S}} \cdot \mathbf{V} \tag{7}$$

which shows that every direction orthogonal to $\dfrac{\delta \mathbf{N}}{\delta \mathbf{S}}$ is conjugate to $\mathbf{t}^{i}$ and conversely. Therefore the 2nd, 3rd,.... $(n-1)$th binormals of the geodesic along $\mathbf{t}$ are conjugate to $\mathbf{t}^{i}$. If $\mathbf{N}_{1/}{}^{\alpha}$, the first binormal is also conjugate to $\mathbf{t}^{i}$, $\tau_2 = 0$ and so $\mathbf{t}^{i}$ is a principal direction. Thus

THEOREM 2.—*If every direction orthogonl to $\mathbf{t}^{i}$ is conjugate to it, or, if every direction conjugate to $\mathbf{t}^{i}$ is orthogonal to it, then $\mathbf{t}^{i}$ is a principal direction in V_n and conversely.*

This compares with the property of the principal directions as the only orthogonal conjugate directions, in ordinary differential geometry.

Now if ω is the angle between $\mathbf{N}^{\alpha}$and $\xi_{1/}{}^{\alpha}$,

$$\cos\omega = \mathbf{N}\cdot\xi_{1/}$$

Taking the intrinsic derivative of both sides along the curve C,

$$\begin{aligned} -\sin\omega\,\frac{d\omega}{ds} &= \mathbf{N}\cdot\frac{\delta\xi_{1/}}{\delta s} + \xi_{1/}\cdot\frac{\delta \mathbf{N}}{\delta s} \\ &= \mathbf{N}\cdot[\mathbf{K}_2\xi_{2/} - \mathbf{K}_1\mathbf{T}] + \xi_{1/}(\cdot\tau_2\mathbf{N}_{1/} - \tau_1\mathbf{T}) \\ &= \mathbf{K}_2(\mathbf{N}\cdot\xi_{2/}) + \tau_2(\xi_{1/}\cdot\mathbf{N}_{1/}). \end{aligned}$$

$$\therefore\quad \underline{\frac{d\omega}{ds} + k_2\frac{\mathbf{N}\cdot\xi_2}{\sin\omega} = -\tau_2\frac{\xi_{1/}\cdot\mathbf{N}_{1/}}{\sin\omega}}. \tag{8}$$

This is a generalization of the well-known formula for " geodesic torsion " $\tau_g = \left(\dfrac{d\omega}{ds} + \dfrac{1}{\sigma}\right)$ in ordinary differential geometry.

If $\mathbf{t}^i$ is an asymptotic direction $\cos\omega = 0$, for the intrinsic derivative in V_{n+1}, i.e., the direction of $\xi_{1/}{}^{\alpha}$ is tangential to V_n so that

$$\underline{k_2\,(\mathbf{N}\cdot\xi_{2/}) = -\,\tau_2\,(\xi_{1/}\cdot\mathbf{N}_{1/}).} \tag{9}$$

Next $$-\,\Omega_{ij}\,\mathbf{t}^i\mathbf{v}^j = \frac{\delta\mathbf{N}}{d\mathbf{S}}\cdot\mathbf{V} = (\tau_1{}^2+\tau_2{}^2)^{\frac{1}{2}}\cos\phi,$$

where ϕ is the angle between V^{α} and the intrinsic derivative of unit normal to the surface along $\mathbf{t}^i$.

Interchanging $\mathbf{v}^j$ and $\mathbf{t}^i$,

$$-\,\Omega_{ij}\mathbf{t}^i\mathbf{v}^j = (\tau_1{}'^2+\tau_2{}'^2)^{\frac{1}{2}}\cos\phi',$$

where ϕ' is the angle between $\mathbf{t}^i$ and the intrinsic derivative of $\mathbf{N}^{\alpha}$ along $\mathbf{v}^i$ and $\tau_1{}'$ and $\tau_2{}'$ refer to the direction $\mathbf{V}^{\alpha}$ so that

$$\underline{(\tau_1{}^2+\tau_2{}^2)\cos^2\phi = (\tau_1{}'^2+\tau_2{}'^2)\cos^2\phi'} \tag{10}$$

If $\mathbf{t}^i$ and $\mathbf{v}^i$ are asymptotic directions, $\tau_1 = \tau_1{}' = 0$ and ϕ is the angle between $\mathbf{V}^{\alpha}$ and $\mathbf{N}_{1/}{}^{\alpha}$. Therefore

$$\underline{\tau_2\cos\phi = \tau_2{}'\cos\phi'} \text{ or } \underline{\tau_2 : \tau_2{}' = \cos\phi' : \cos\phi} \tag{11}$$

Let k_2', $\xi_{1/}{}'^{\alpha}$, $\xi_{2/}{}'^{\alpha}$ and $\mathbf{N}_{1/}{}'{}^{\alpha}$ denote corresponding quantities for the asymptotic direction $\mathbf{v}^i$. Writing down the equation for the direction $\mathbf{v}^i$ corresponding to equation (9) and eliminating τ_2 and $\tau_2{}'$ from this equation, equations (9) and (11), we obtain

$$\frac{\mathrm{K}_2}{\mathrm{K}_2{}'} + \frac{(\xi_{1/}\cdot\mathbf{N}_{1/})}{(\xi_2\cdot\mathbf{N})}\cdot\frac{(\xi_{2/}{}'\cdot\mathbf{N})}{(\xi_{1/}{}'\cdot\mathbf{N}_{1/}{}')}\cdot\frac{\cos\phi}{\cos\phi'}.$$

If we write $\xi_{1/}\cdot\mathbf{N}_{1/} = \cos\omega_1$, $\xi_{2/}\cdot\mathbf{N} = \cos\omega_2$, $\xi_{2/}{}'\cdot\mathbf{N} = \cos\omega_2{}'$ and $\xi_{1/}{}'\cdot\mathbf{N}' = \cos\omega_1{}'$, the above equation takes the form

$$\underline{\frac{\mathrm{K}_2}{\mathrm{K}_2{}'} = \frac{\cos\omega_1}{\cos\omega_2}\cdot\frac{\cos\omega_2{}'}{\cos\omega_1{}'}\cdot\frac{\cos\phi}{\cos\phi'}} \tag{12}$$

This can be looked upon as a generalization of Enneper's formula connecting torsions of asymptotic lines in ordinary differential geometry, where $\cos\omega_1$, $\cos\omega_2$, $\cos\omega_1{}'$ and $\cos\omega_2{}'$ each reduce to unity and $\cos\phi/\cos\phi' = -1$.

If $\mathbf{T}^{\alpha}$ and $\mathbf{V}^{\alpha}$ are orthogonal vectors

$$-\,\Omega_{ij}\mathbf{t}^i\mathbf{v}^j = \mathbf{V}\cdot(\mathbf{N}_{1/}\tau_2 - \mathbf{T}\tau_{1/}) = \tau_2\cos\psi$$

$$\text{and similarly, } = \tau_2{}'\cos\psi'$$

where ψ is the angle between $\mathbf{V}^{\alpha}$ and $\mathbf{N}_{1/}{}^{\alpha}$ and ψ' defined similarly. So we have

$$\underline{\tau_2\cos\psi = \tau_2{}'\cos\psi',\ i.e.,\ \tau_2 : \tau_2{}' = \cos\psi' : \cos\psi.} \tag{13}$$

Results (11) and (13) can be together stated as follows:

The torsions of geodesics in two asymptotic directions or in any two orthogonal directions are in the ratio of the cosine of the angle between the first direction and the first binormal to the geodesic in the second direction and the cosine of the angle between the second direction and the first binormal to the geodesic in the first direction.

In ordinary differential geometry one of ψ, ψ' of (13) is zero and the other is π.

5. Lastly we obtain some relations between the curvatures of C in V_n.

$$\frac{\delta \mathbf{B}_{1_l}{}^{\alpha}}{ds} = (\Omega_{ij}\mathbf{b}_{1_l}{}^{i}\mathbf{t}^{j})\,\mathbf{N}^{\alpha} + \frac{\delta \mathbf{b}_{1_l}{}^{i}}{\delta s}\,y_{;i}{}^{\alpha}$$

$$= \left(-\frac{\delta \mathbf{N}}{\delta s}\cdot \mathbf{B}_{1_l}\right)\mathbf{N}^{\alpha} + (c_2\mathbf{b}_2{}^{i} - c_1\mathbf{t}^{i})\,y_{;i}{}^{\alpha}, \text{ by (1) and (7)},$$

$$= [-(\tau_2\mathbf{N}_1 - \tau_1\mathbf{T})\cdot \mathbf{B}_{1_l}]\,\mathbf{N}^{\alpha} + c_2\mathbf{B}_{2_l}{}^{\alpha}, \text{ by (2)}.$$

$$\therefore\quad \frac{\delta \mathbf{B}_{1_l}{}^{\alpha}}{\delta s} = -\tau_2\cos\phi_1\mathbf{N}^{\alpha} + c_2\mathbf{B}_{2_l}{}^{\alpha} - c_1\mathbf{T}^{\alpha},$$

$$\text{and}\qquad \left(\frac{\delta \mathbf{B}_{1_l}}{\delta s}\right)^2 = \tau_2{}^2\cos^2\phi_1 + c_2{}^2 + c_1{}^2., \tag{14}$$

where ϕ_1 is the angle between $\mathbf{N}_{1_l}{}^{\alpha}$ and $\mathbf{B}_{1_l}{}^{\alpha}$. Compare these with the following equations of ordinary differential geometry.

$$\frac{d\mathbf{b}}{ds} = -(k_g\vec{\mathbf{t}} - \tau_g\vec{\mathbf{N}})$$

$$\text{and}\qquad \left(\frac{d\mathbf{b}}{ds}\right)^2 = k_g{}^2 + \tau_g{}^2.$$

Taking the intrinsic derivative of the $(r-1)$th binormal in V_n to C and putting $\mathbf{N}_{1_l}{}^{\alpha} = \sum_{p=1}^{n-1}\cos\phi_p\mathbf{B}_{p_l}{}^{\alpha}$, since $\mathbf{N}_{1_l}{}^{\alpha}$ is in V_n and orthogonal to $\mathbf{T}^{\alpha}$ and $\mathbf{B}_{r_l}{}^{\alpha}$ $r = 1, \ldots, n-1$ are tangential to V_n we obtain the general formulæ

$$\frac{\delta \mathbf{B}_{r_l}{}^{\alpha}}{\delta s} = -(\tau_2\cos\phi_r)\,\mathbf{N}^{\alpha} + c_{r+1_l}\mathbf{B}_{r+1_l}{}^{\alpha} - c_r\mathbf{B}_{r-1_l}{}^{\alpha},$$

$$\text{for } r = 1, \ldots, n-2,$$

$$\text{and}\qquad \frac{\delta \mathbf{B}_{n-1_l}{}^{\alpha}}{\delta s} = -\tau_2{}^2\cos\phi_{n-1}\mathbf{N}^{\alpha} - c_{n-1}\mathbf{B}_{n-2_l}{}^{\alpha}$$

Squaring these,

$$\left(\frac{\delta \mathbf{B}_{r_l}}{\delta s}\right)^2 = \tau_2{}^2\cos^2\phi_r + c^2{}_{r+1} + c_r{}^2,$$

$$\text{for } r = 1, \ldots, n-2,$$

$$\text{and}\qquad \left(\frac{\delta \mathbf{B}_{n-1_l}}{\delta s}\right)^2 = \tau_2{}^2\cos^2\phi_{n-1} + c^2{}_{n-1}. \tag{15}$$

If C is a line of curvature $\tau_2 = 0$ and so $\frac{\delta \mathbf{B}_{r1}{}^{\alpha}}{\delta s}$ is tangential to V_n and equations (15) become

$$\frac{\delta \mathbf{B}_{r1}{}^{\alpha}}{\delta s} = c_{r+1}\mathbf{B}_{r+1}{}^{\alpha} - c_r \mathbf{B}_{r-1}{}^{\alpha} \qquad \text{for } r = 1, \ldots, n-2.$$

$$\frac{\delta \mathbf{B}_{n-1\,1}{}^{\alpha}}{\delta s} = -c_{n-1}\mathbf{B}_{n-2\,1}{}^{\alpha}$$

$$\left(\frac{\delta \mathbf{B}_{r1}}{\delta s}\right)^2 = c_{r+1}{}^2 + c_r{}^2 \qquad \text{for } r = 1, \ldots, n-2$$

$$\left(\frac{\delta \mathbf{B}_{n-1\,1}}{\delta s}\right)^2 = c_{n-1}{}^2$$

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1. Weatherburn .. *Riemannian Geometry*, p. 95.
2. ———— .. *Ibid.*, p. 128, equation (14).
3. ———— .. *Ibid.*, p. 137.
4. ———— .. *Ibid.*, p. 133, equation (30).
5. ———— .. *Ibid.*, p. 136, equation (42).

Post-Script.—Since the communication of this paper, the following extension of formula (5) for a subspace V_n in a Riemannian V_m has been obtained.

$$\tau_2{}^2 = \tfrac{1}{2} \sum_{p=1}^{n} \sum_{q=1}^{n} \cos^2 \phi_p \cos^2 \theta_q \left(\frac{1}{\rho_p} - \frac{1}{\rho_q}\right)^2 + \sum_{h=2}^{m-n} \theta_{1h}{}^2,$$

where $\theta_{1h} = [(\mathbf{N}_{1;i} e^i) \cdot \mathbf{N}_{h1}]$, $\mathbf{N}_1{}^{\alpha}$ being the principal normal to the geodesic along $\mathbf{t}^i$, $\cos \theta_p$ being the scalar product of $\mathbf{t}^i$ and unit vectors along the principal directions corresponding to the normal $\mathbf{N}_1{}^{\alpha}$. The unit vectors $\mathbf{N}_{11}{}^{\alpha}, \ldots, \mathbf{N}_{m-n}{}^{\alpha}$ are the mutually orthogonal normals to V_n. The proof of this result is on similar lines.

STUDIES ON NIOBIUM AND TANTALUM

Part IV. Polynuclear Complexes

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Introduction

The isolation and study of tartratoniobic acid and the tartratoniobates of the alkali, alkaline earth and other metals have been described in detail by this author in this journal (1950). It has been found that, as in phosphomolybdates and in arsenomolybdates, degradation takes place in some of the compounds giving rise to new polynuclear complexes of niobium. This paper deals with the preparation and study of a new series of salts as also of the free acid.

Experimental

Degradation Studies.—During the preparation of the tartratoniobates of the alkali metals, it was observed that variable values for tartaric acid were encountered in the compounds, depending on the mode of their preparation. When solutions containing the 2-tartrato-2-niobates were boiled for a long time, the products obtained contained less of tartaric acid. Thus, sodium (7 : 6) niobate was reacted with tartaric acid and after removal of the sodium hydrogen tartrate formed, the filtrate was kept boiling for 2 hours. The crystals that were obtained on cooling, analysed to the composition given in Table I.

Table I

	Found %
Na_2O ..	8·76
Nb_2O_5 ..	41·29
$C_4H_4O_5$ ..	35·89
H_2O ..	14·06

Table II

	1st Crop Found %	2nd Crop Found %
Na_2O ..	9·04	8·9
Nb_2O_5 ..	41·55	34·6
$C_4H_4O_5$ ..	31·12	35·2
H_2O ..	18·29	21·3

On calculation it was seen that the ratio of Nb_2O_5 to $C_4H_4O_5$ was as 1 : 1·75. To find out the homogeneity of the substance, it was recrystallised from water, when two crops were obtained. They were analysed in the customary way with the results given in Table II.

In the first crop there exists a ratio of Nb_2O_5 : $C_4H_4O_5$ as 1 : 1·5 while in the second the ratio is 1 : 2. The composition did not change on subsequent crystallisation of the two substances. The second crop is the 2-sodium-2-tartrato-2-niobate met with already. The first is formulated as another complex compound of niobium, the theoretical requirements for which are given in Table III.

TABLE III

	Found %	Calculated for $2\,Na_2O.2\,Nb_2O_5\cdot(C_4H_4O_5)_3.13\,H_2O$ %
Na_2O	9·04	9·65
Nb_2O_5	41·55	41·38
$C_4H_4O_5$	31·12	30·82
H_2O	18·29	18·15

The compound prepared has therefore the formula

$2\,Na_2O\cdot2\,Nb_2O_5\,(C_4H_4O_5)_3\cdot13\,H_2O$, and can be named as 4-sodium-3-tartrato-4-niobate 13-hydrate.

The preparation of the above compound was also attempted from sodium (1 : 1) niobate by reaction with tartaric acid. $Na_2O\cdot Nb_2O_5\cdot7\,H_2O$ (1 g.) was dissolved in water (20 ml.) and tartaric acid (0·8 g.) added. The mixed solution remained clear. The solution was boiled for 2 hours and cooled in ice. No crystals separated and therefore recourse was taken to crystallisation with the addition of alcohol. A white substance separated instantaneously, which was filtered, washed with alcohol, dried (1·5 g.) and analysed. The alcoholic filtrate was found to contain only free tartaric acid (0·33 g.). Results in Table IV.

Therefore the compound is the same as prepared earlier and is of the formula $2\,Na_2O\cdot2\,Nb_2O_5\cdot(C_4H_4O_5)_3\cdot13\,H_2O$.

When the previous experiment was conducted employing an excess of tartaric acid, the solid separated by alcohol precipitation, had the same

TABLE IV

	Found %	Calculated for $2\,Na_2O.2\,Nb_2O_5.(C_4H_4O_5)_3.13\,H_2O$ %
Na_2O	9·69	9·65
Nb_2O_5	42·02	41·38
$C_4H_4O_5$	30·66	30·82
H_2O	17·63	18·15

composition as shown in the previous table. This shows clearly that, even in presence of excess of tartaric acid, the effect of prolonged boiling is only to favour the formation of the 4-sodium-3-tartrato-4-niobate.

Potassium Compound.—The effect of prolonged heating on potassium-2-tartrato-2-niobate was studied and results analogous to those of the sodium compound were obtained. Recrystallised potassium (4: 3) niobate (3 g.) was reacted with tartaric acid (3·6 g.) and the potassium hydrogen tartrate formed removed. The filtrate was boiled vigorously for 2 hours, when it become highly viscous and turned into a transparent jelly. The solution was cooled and the solid separated by the addition of alcohol. The product was analysed when the results were obtained as in Table V.

TABLE V

	Found %	Calculated for $2\,K_2O.2\,Nb_2O_5.(C_4H_4O_5)_3.13\,H_2O$ %
K_2O	13·6	13·96
Nb_2O_5	39·45	39·40
$C_4H_4O_5$	29·68	29·34
H_2O	17·27	17·30

The compound that has been obtained can be formulated as $2\,K_2O{\cdot}2\,Nb_2O_5{\cdot}(C_4H_4O_5)_3{\cdot}13\,H_2O$, and named as 4-potassium-3-tartrato-4-niobate 13-hydrate. The experiment was repeated several times and identical results were obtained.

When a solution of 2-tartrato-2-niobate is vigorously boiled, hydrolytic decomposition takes place with the splitting up of tartaric acid and consequent production of salts poorer in tartaric acid. In the experiments that follow the actual amount of tartaric acid liberated is determined with a view to estimating the extent of hydrolytic decomposition.

$K_2O \cdot Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10\ H_2O$ (1 g.) was dissolved in hot water (25 ml.) and the solution kept vigorously boiling for one hour. The solution was cooled and the substance precipitated with an excess of alcohol, stirred well, filtered and washed with alcohol. The clear filtrate was analysed for tartaric acid by titration with standard NaOH.

Tartaric acid found $= 0{\cdot}0797$ g. Theoretical $= 0{\cdot}0933$ g. It can be seen that in this case, decomposition takes place only to the extent of $85{\cdot}5\%$; probably more time is required for it to go to completion.

The reversibility of the reaction that is described above was tested in the following manner by repeatedly removing the tartaric acid formed during the decomposition of the 2-tartrato-2-niobate on heating. One g. of the same compound was taken in 25 ml. water, boiled vigorously for 30 minutes, cooled, the substance precipitated with alcohol, filtered and washed. Tartaric acid was estimated in the alcoholic filtrate as described previously. The precipitate was retaken in water, boiled for another 30 minutes and the amount of tartaric acid formed estimated. The procedure was repeated several times and the results are given in Table VI.

TABLE VI

No. of times heated	Duration of heating mts.	Tartaric acid expelled g.	Total tartaric acid expelled g.
1	30	0·03071	0·03071
2	30	0·02639	0·05710
3	30	0·02433	0·08143
4	30	0·01238	0·09381

It can be seen that repeated vigorous boiling for 2 hours results in expelling almost the theoretical amount of tartaric acid while by continuous heating for one hour only a lesser amount of tartaric acid can be expelled. This shows that the reaction is not reversible but that there is spontaneous

hydrolytic decomposition of the 2-tartrato-2-niobate into the 3-tartrato-4-niobate.

Since keeping the 2-tartrato-2-niobate at elevated temperatures enabled it to decompose with the formation of the 3-tartrato-4-niobate, attempts were made to prepare the original compound, *viz.*, 2-tartrato-2-niobate by keeping the 3-tartrato-4-niobate with excess of tartaric acid at low temperatures. There was very little absorption of tartaric acid at room temperatures; keeping the solution for periods ranging from 1 to 7 days, at 5° C. in a refrigerator and subsequent analysis, revealed that the 3-tartrato-4-niobate had not undergone any chemical change. It becomes evident that even at low temperatures, tartaric acid and 3-tartrato-4-niobate do not react to give the 2-tartrato-2-niobate and that once the former compound is formed it is difficult to reconvert it into the latter.

Ammonium compound.—Literature does not reveal the existence of any ammonium niobate and hence the corresponding tartratoniobate could not be prepared by the general method mentioned previously for the alkali metal compounds. The following method was adopted in preparing the ammonium compound. Freshly precipitated niobium pentoxide was suspended in water (50 ml.) and ammonium hydrogen tartrate (3 g.) added to the suspension and heated over the water-bath. After about 2 hours the solution became clear but had a slight yellowish tinge. The solution was concentrated to about half its volume and cooled in ice. Ammonium hydrogen tartrate separated as white crystals. On further concentration and cooling ammonium hydrogen tartrate separated till the volume was reduced to 12 ml. At this stage the crystals contained appreciable quantities of niobium. The solution reduced to 5 ml. was viscous and could not be crystallised. Hence the solid was separated by crystallisation with the aid of alcohol and analysed in the usual way with the results given in Table VII.

TABLE VII

	Found %	Calculated for $2(NH_4)_2O.2Nb_2O_5.(C_4H_4O_5)_3.12H_2O$ %
$(NH_4)_2O$	8·12	8·34
Nb_2O_5	42·77	42·61
$C_4H_4O_5$	31·65	31·74
H_2O	17·46	17·31

Therefore the ammonium complex prepared corresponds to the formula $2(NH_4)_2O \cdot 2Nb_2O_5 \cdot (C_4H_4O_5)_3 \cdot 12\ H_2O$, and can be named in the customary manner as 4-ammonium-3-tartrato-4-niobate-12-hydrate.

3-*Tartrato*-4-*niobic acid.*—The free acid corresponding to the above mentioned 3-tartrato-4-niobates has also been isolated. 2-Tartrato-2-niobic acid 10-hydrate obtained earlier in this work (Part I) was dissolved in water and the solution kept boiling for 2 hours. The solution was cooled and the substance crystallised out in the usual way with the addition of alcohol and analysed for niobium, tartaric acid and water by the procedure described already. The results obtained are summarised in Table VIII.

TABLE VIII

	Found %	Calculated for $2\ Nb_2O_5 \cdot (C_4H_4O_5)_3 \cdot 16\ H_2O$ %
Nb_2O_5	43·8	43·75
$C_4H_4O_5$	32·88	32·58
H_2O	23·32	23·67

The compound obtained is 3-tartrato-4-niobic acid 16-hydrate of the composition $2\ Nb_2O_5 \cdot (C_4H_4O_5)_3 \cdot 16\ H_2O$.

Alkali titrations of tartratoniobates.—The tartratoniobic acids and alkali tartratoniobates were titrated against standard sodium hydroxide using phenolphthalein as indicator. It was observed that the reaction proceeded slowly in the cold and hence the titrations were completed in hot after boiling the solutions when the end-points were sharp and the pink colour remained steady. It should, however, be mentioned here that potentiometric titrations with tartratoniobic acids and sodium hydroxide were tried when serious difficulties were met with. The e.m.f.'s recorded after each addition of alkali hydroxide were fluctuating considerably, owing to the very slow attainment of equilibrium in the cold, which vitiated the results. Table IX summarises the results of the direct alkali titrations.

It can be seen that the 2-tartrato-2-niobates consume four equivalents of sodium hydroxide, due to the formation of alkali tartrates consequent on the breakdown of the complex with the simultaneous formation of alkali niobate. The products of decomposition have been identified as the alkali niobate and the alkali tartrate. The 3-tartrato-4-niobates, similarly, require six equivalents of sodium hydroxide.

TABLE IX

Substance	Weight g.	Ml. NaOH 0·09165 N	Equivalents of NaOH per gm. mol.
$Na_2O.Nb_2O_5.(C_4H_4O_5)_2.10\ H_2O$	0·1827	10·15	3·93
$K_2O.Nb_2O_5.(C_4H_4O_5)_2.10\ H_2O$	0·3308	17·9	3·98
$Li_2O.Nb_2O_5.(C_4H_4O_5)_2.8\ H_2O$	0·2120	13·2	4·02
$2\ Na_2O.2\ Nb_2O_5.(C_4H_4O_5)_3.13\ H_2O$ ..	0·2140	10·9	6·00
$2\ K_2O.2\ Nb_2O_5.(C_4H_4O_5)_3.13\ H_2O$ ..	0·3424	16·8	6·05
$2(NH_4)_2O.2\ Nb_2O_5.(C_4H_4O_5)_3.12\ H_2O$ ..	0·2657	13·75	5·91
$Nb_2O_5.(C_4H_4O_5)_2.10\ H_2O$ (Cold)	0·1316	8·05	3·98
$Nb_2O_5.(C_4H_4O_5)_2.10\ H_2O$ (Hot)	0·1001	7·73	5·02
$2\ Nb_2O_5.(C_4H_4O_5)_3.16\ H_2O$	0·2349	12·7	6·02

The 2-tartrato-2-niobic acid consumes four equivalents of sodium hydroxide which accounts for the formation of the alkali tartrate. However, on boiling, one more equivalent is consumed which probably may be due to the dissolving of niobic acid in alkali hydroxide. The solution remains clear. The same reasoning holds good for the 3-tartrato-4-niobic acid also.

The alkaline earth tartratoniobates when treated with dilute alkali hydroxide decompose and begin to precipitate niobium pentoxide, the alkaline earth metal tartrates being formed in solution. The precipitation of niobium pentoxide is slow in the calcium salt whereas it is almost instantaneous in the case of the barium salt.

DISCUSSION

It has been shown that when a solution of 2-sodium-2-tartrato-2-niobate is vigorously boiled for two hours, tartaric acid is expelled with the formation of a compound poorer in tartaric acid, *viz.*, 4-sodium-3-tartrato-4-niobate. The following equation is envisaged:

$$2\ [Na_2O.Nb_2O_5.(C_4H_4O_5)_2.aq.] + H_2O \rightarrow$$
$$2\ Na_2O.2\ Nb_2O_5.(C_4H_4O_5)_3 + C_4H_6O_6.$$

2-potassium-2-tartrato-2-niobate behaves identically. The free acid corresponding to the 3-tartrato-4-niobates has also been isolated by decomposition of the 2-tartrato-2-niobic acid. Studies made on the liberation of tartaric acid revealed that the reaction is spontaneous and irreversible. It is recognised that the degradation of the 2-tartrato-2-niobates has been brought about by the hydrolytic action of water under the influence of heat. The 3-tartrato-4-niobates consequently formed can be regarded as polynuclear complexes.

The degradation explained above can be supported from the fact that there is a progressive decomposition noticed in the molybdophosphates (Ephraim, 1943). The compound of the formula $R_2O \cdot P_2O_5 \cdot 24\ M_0O_3$ gradually decomposes through a series of stages resulting finally in a compound $R_2O \cdot P_2O_5 \cdot 2MoO_3$. Further there is a progressive gradation in the stability of many of the complex compounds and the stability decreases as shown in the following scheme. $Si \rightarrow P \rightarrow As \rightarrow Bi \rightarrow V$. Since it is known that the complexity of the niobates corresponds to that of the vanadates, Nb can be put next to V in the above scheme. Moreover, since the heteropoly acids are susceptible to heat, it can be expected that the heteropoly acids of niobium would be unstable. Thus the formation of the 3-tartrato-4-niobates can be accounted, and postulated as polynuclear complexes. Examples of polynuclear complexes amongst heteropoly acids are many and mention may be made of the following prepared by Rosenheim (1921), *viz.*, $Na_4\,[Cu_4(B_4O_7)_6]\ 50\ H_2O$, $Cs_{12}\,[As_2\,(Mo_2O_7)\ O_2]\ 5\ H_2O$ and $Ag_{22}\,[P_4\,(Mo_2O_7)_{17}O_4]\ 40\ H_2O$. Therefore the 3-tartrato-4-niobates can also be treated as polynuclear complexes and assigned the structure given below:

3-Tartrato-4-niobic acid 16-hydrate.

$$2\ Nb_2O_5 \cdot (C_4H_4O_5)_3 \cdot 16\ H_2O.$$

$$H_4\left[\begin{array}{ccc} & O_9 & \\ Nb_4 & & (H_2O)_{12} \\ & (C_4H_4O_6)_3 & \end{array}\right] 2\ H_2O.$$

The alkali and ammonium salts can be represented by the general formula:

$$M_4\left[\begin{array}{ccc} & O_9 & \\ Nb_4 & & (H_2O)_{12} \\ & (C_4H_4O_6)_3 & \end{array}\right] n\ H_2O$$

where M = Na, K or NH_4 and n = varying number.

Summary

It has been found that in aqueous solutions, on vigorous boiling, the 2-tartrato-2-niobates and the corresponding free acid are degraded, giving rise to new complexes of niobium. The conditions of formation and the mechanism of the reaction have been studied. Adequate explanation has been offered for the phenomenon. The compounds are regarded as polynuclear complexes and suitable structures are given for the compounds prepared.

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SYNTHETIC EXPERIMENTS IN THE BENZOPYRONE SERIES

Part XIX. Methyl Ethers of Genistein*

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and
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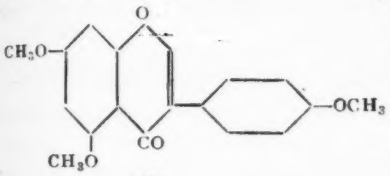
Received May 24, 1952

Of the three possible monomethyl ethers of genistein the 4′-methyl ether was synthesised by Shriner and Hull[1] and soon after this synthesis it was also found to occur in nature as biochanin-A.[2] Another earlier known naturally occurring monomethyl ether, prunetin was therefore considered to be the 7-methyl ether of genistein and this constitution was confirmed by later synthetic work. Narasimhachari and Seshadri[3] prepared its diethyl ether and showed that it was identical with 7-methoxy-5: 4′-diethoxy isoflavone obtained by independent synthesis. The synthesis of prunetin itself was first reported by Iyer, *et al.*,[4] using 2-hydroxy-4: 6-dimethoxy-4′-nitrophenyl-benzyl ketone and passing through a number of stages. A simplified synthesis was given by Kotake and Fukui[5] who employed 2: 4′-dihydroxy-4: 6-dimethoxy-phenyl-benzyl ketone for the isoflavone condensation. An even simpler method however, is the direct partial methylation of genistein to prunetin reported by Narasimhachari and Seshadri[3] and this is also significant biogenetically.

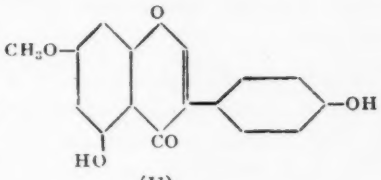
The schemes of synthesis adopted by Iyer, *et al.*[4] and Kotake and Fukui[5] seem to have been based on the assumption that there should be difficulty in the partial demethylation of isoflavones just as in the case of flavones, that it should be particularly difficult to demethylate the 4′-position without affecting the 7-position and that even for the partial hydrolysis of the 5-methyl ether group leaving out the 7-methoxyl group, mild conditions are necessary. In a previous part of this series[6] this question has been specially examined and the experimental results (preparation of isoformononetin and 7-methoxy-5-hydroxy isoflavone) were described leading to the conclusion that the 7-methoxyl is markedly far more resistant than the others enabling even the use of hydriodic acid for the partial demethylation. In further support

* A preliminary note on this subject was published in the *J. Sci. Ind. Res. India*, 1951, **10B** 195.

of this contention the demethylation of genistein trimethyl ether (I) has now been carried out using hydrobromic acid and hydriodic acid and good yields of prunetin (II) obtained. This now provides the simplest synthetic method of preparing this substance.

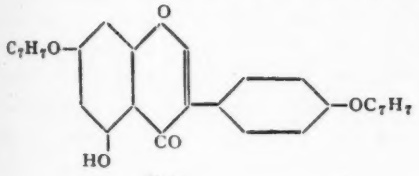


(I)



(II)

The third methyl ether of genistein now named isoprunetin (III) (5-O-methyl genistein) has also now been made. For this purpose genistein is first benzylated to yield the dibenzyl ether (IV). The reactions of this compound are in agreement with the presence of a free 5-hydroxyl group. Subsequent methylation (V) and debenzylation yields isoprunetin (III). The identity of this compound is established by its complete ethylation. The product is found to be identical with 5-methoxy-7: 5′-diethoxy isoflavone (VI) prepared through 7: 4′-diethyl ether of genistein (VII) as intermediate. This diethyl ether of genistein was first reported by Perkin and Horsfall[7]



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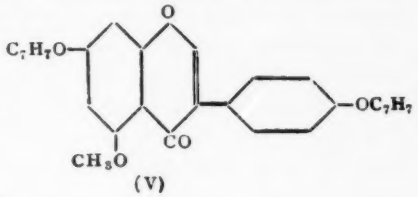

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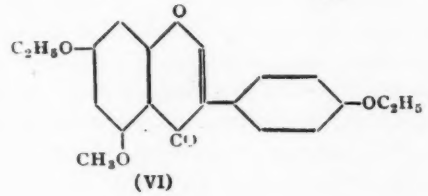

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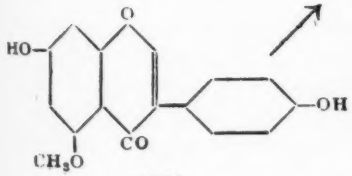
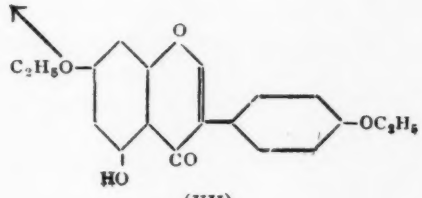


(III)



(VII)

who expressed that they had difficulties in getting it pure by using alcoholic potash and ethyl iodide for ethylation. The melting point recorded by them is somewhat low. It has now been obtained more easily by ethylating genistein with ethyl iodide (2 moles) and potassium carbonate in acetone solution. Further methylation of it yields 5-methoxy-7: 4′-diethoxy isoflavone (VI).

In their examination of the bark of *Prunus puddum* Chakravarti and Bhar[1] obtained a genistein monomethyl ether having a somewhat lower melting point than prunetin; its acetate was also found to have a lower melting point than prunetin acetate. Further they reported that it did not undergo partial methylation yielding its monomethyl ether. They could only get its dimethyl ether which was identical with genistein trimethyl ether. Consequently they came to the conclusion that it was a new substance having the constitution of the 5-monomethyl ether of genistein and gave it the name prunusetin. Narasimhachari and Seshadri[9] pointed out that this conclusion was erroneous because the substance gave a brownish violet colouration with ferric chloride and because it was insoluble in aqueous sodium carbonate. They further showed that by careful purification the melting points of the substance and its acetate could be raised to those of prunetin and its acetate respectively and that partial methylation could be accomplished by using one mole of dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone medium. The product, a dimethoxy compound had the same melting point and properties as monomethyl prunetin. They stated therefore that there was no doubt that prunusetin was essentially prunetin though slightly impure and the new name was not necessary. In spite of these evidences, Chakravarti and Sen[10] expressed the feeling that their original claim might be correct. Subsequently our experiments[4] on ethylation using this sample of prunetin from *Prunus puddum* was reported and the diethyl ether was found to be identical with 7-methoxy-5: 4′-diethoxy isoflavone. To these evidences we may now add the results reported in this paper on the preparation and properties of the 5-methyl ether of genistein; there is absolutely no agreement between the recorded properties of prunusetin and of the 5-methyl ether of genistein (isoprunetin) whereas there is close resemblance between prunusetin and prunetin. In our earlier paper[9] we have emphasised that there should be marked difference between the 5-methyl ether of genistein and prunetin, the 7-methyl ether. The former was expected to have a higher melting point, to be soluble in sodium carbonate and not give ferric chloride colour. All these expectations are found to be correct as could be seen from the data presented in the following table.

TABLE

	Prunetin (7-O-methyl genistein)	Prunusetin	Isoprunetin (5-O-methyl genistein)
1. Melting point	240–42°	237–38°	284–86°
2. Acetate	224–26°	220–22°	168–70°
3. Ferric chloride	Violet	Violet	Nil
4. Solubility in sodium carbonate	Insoluble	Insoluble	Soluble

EXPERIMENTAL

Demethylation of genistein trimethyl ether

(1) *With hydrobromic acid.*—Genistein trimethyl ether[3] (0·5 g.) was dissolved in glacial acetic acid (10 c.c.) and the solution treated with aqueous hydrobromic acid (d. 1·51; 10 c.c.). The mixture was heated in a boiling water-bath for 3 hours. It was then cooled, diluted with water and the solid product filtered and washed with water. It readily dissolved in cold aqueous sodium hydroxide; the solution was filtered from a small resinous impurity and the clear alkaline solution acidified. The product crystallised from alcohol as colourless needles melting at 238–40°. Yield 0·35 g. It was identical in every respect with prunetin and a mixed melting point with an authentic sample[9] was undepressed. The acetate crystallised from ethyl acetate as rhombohedral prisms melting at 223–25° alone or in admixture with a sample of prunetin acetate.

(2) *With hydriodic acid.*—On demethylation with hydriodic acid in acetic anhydride solution at 140° for one hour (*cf.* Narasimhachari and Seshadri[11]) a mixture of prunetin and genistein was obtained and the separation could be effectively carried out using sodium carbonate in which the former is insoluble. From 1 g. of the trimethyl ether 0·25 g. of prunetin could be obtained.

By carrying out the demethylation at 120° for half an hour[6] an almost quantitative yield of prunetin was obtained. After the product was washed with aqueous sodium carbonate it crystallised from alcohol as colourless prisms melting at 238–40° (mixed m.p. with prunetin undepressed) and gave an acetate identical with prunetin acetate (m.p. and mixed m.p. 223–25°). The carbonate solution on acidification gave only a trace of genistein.

Genistein-7: 4'-dibenzyl ether

Genistein (1·5 g.) was refluxed in acetone solution (250 c.c.) with benzyl chloride (1·3 c.c.) and anhydrous potassium carbonate (8 g.) for 20 hours. Acetone was then distilled off and the residue treated with water. The solid that separated was filtered and washed with water. 7: 4'-O-dibenzyl genistein crystallised from ethyl acetate as colourless tiny prisms melting at 190–92°. It gave a red colour with ferric chloride and was sparingly soluble in aqueous sodium hydroxide. It was not easily soluble in alcohol and acetone. Yield, 1·5 g. (Found: C, 76·9; H, 5·2; $C_{29}H_{22}O_5$ requires C, 77·3; H, 4·9%).

7: 4'-*Dibenzyloxy-5-methoxy isoflavone*

The above compound (1·5 g.) was methylated by refluxing with dimethyl sulphate (0·5 c.c.) and anhydrous potassium carbonate (2 g.) in acetone (200 c.c.) for 20 hours. The solvent was then distilled off and water added to the residue. The colourless solid that separated was filtered, washed with water and crystallised from ethyl acetate. 7: 4'-Dibenzyloxy-5-methoxy isoflavone was obtained in the form of colourless rectangular plates and needles and melted at 189–90°. It gave no colour with ferric chloride and was insoluble in aqueous sodium hydroxide (Found: C, 77·2; H, 5·2; $C_{30}H_{24}O_5$ requires C, 77·6; H, 5·2%).

5-O-*Methyl genistein* (*isoprunetin*)

A suspension of the dibenzyl methyl ether (1 g.) in glacial acetic acid (10 c.c.) was treated with concentrated hydrochloric acid (10 c.c.) and the mixture heated in a boiling water-bath for one hour. It was filtered hot to separate the unchanged benzyl ether and the filtrate diluted with water. The solid product that separated on cooling was filtered and washed with water and small quantities of petroleum ether. It was then dissolved in aqueous sodium carbonate and the solution filtered. The clear filtrate when acidified gave 5-O-methyl genistein as a colourless solid. It was crystallised from ethyl acetate-alcohol mixture when it separated in the form of colourless rectangular plates and prisms melting at 284–86°. It was acetylated with acetic anhydride and pyridine and the acetate on crystallising from ethyl acetate was obtained as colourless rectangular plates melting at 169–70° (Found: C, 65·0; H, 4·0; OCH_3 8·1; $C_{20}H_{16}O_7$ requires C, 65·2; H, 4·3; OCH_3 8·4%). The pure acetate was deacetylated with alcoholic hydrochloric acid and the product crystallised from ethyl acetate-alcohol mixture. 5-O-Methyl genistein separated in the form of colourless

rectangular plates and prisms melting at 284–6°. It dissolved readily in aqueous sodium carbonate and sodium hydroxide and gave no colour with ferric chloride (Found: C, 65·6; H, 4·8; OCH_3 9·9; $C_{16}H_{12}O_5$, $\frac{1}{2}H_2O$ requires C, 65·5; H, 4·5%; OCH_3 10·6%). Yield 0·2 g.

5-Methoxy-7: 4′-diethoxy isoflavone

(1) *Ethylation of isoprunetin.*—5-O-Methyl genistein (0·2 g.) was refluxed in acetone solution with ethyl iodide (0·5 c.c.) and anhydrous potassium carbonate (2 g.) for 6 hours. On filtering the mixture and distilling off the solvent from the filtrate the ethyl derivative was obtained as a colourless solid. It crystallised from ethyl acetate as colourless stout rhombic prisms and melted at 120–21°. It was identical with 7: 4′-diethoxy-5-methoxy isoflavone obtained from genistein according to the method described below and the mixed melting point was not depressed.

(2) *Methylation of* 7: 4′-O-*diethyl genistein.*—Genistein 7: 4′-diethyl ether was prepared by ethylating genistein with ethyl iodide (2 moles) and potassium carbonate in acetone solution. It crystallised from alcohol as colourless lens-shaped crystals melting at 139–40° (Perkin and Horsfall[7] reported 132–34°). It gave a red colour with ferric chloride and was sparingly soluble in aqueous alkali (Found: C, 69·8; H, 5·6; $C_{19}H_{18}O_5$ requires C, 69·9; H, 5·5%). Its acetate crystallised from alcohol as colourless needles melting at 171–2° (Perkin and Horsfall[7] gave m.p. 168–70°).

Genistein-7: 4′-diethyl ether was boiled with excess of dimethyl sulphate and potassium carbonate in acetone solution for 20 hours; 5-Methoxy-7: 4′-diethoxy isoflavone crystallised from ethyl acetate as colourless stout rhombic prisms melting at 120–21°. It was insoluble in aqueous alkali and gave no colour with ferric chloride (Found: C, 71·0; H, 5·9; $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

Summary

It is shown that the most convenient method of preparing prunetin is by the partial demethylation of genistein trimethyl ether with hydrobromic or hydriodic acid under controlled conditions. The 5-methyl ether of genistein (isoprunetin) has now been synthesised by the methylation of 7: 4′-O-dibenzyl genistein and subsequent debenzylation. Its properties are very different from those of prunetin and it yields a diethyl ether which could be independently prepared from genistein. The present work conclusively proves that prunusetin cannot be 5-O-methyl genistein (isoprunetin) and should be the same as prunetin.

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KINETIC STUDIES IN ESTER HYDROLYSIS

Part VII. Solvent Influences

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In earlier parts of the series we had reported in these *Proceedings*, the results of our studies on the hydrolysis of ethyl acetate in different solvent mixtures and of other esters in 60% dioxan.[2, 3] It is necessary at this stage to consider the extent and probable manner in which the solvent affects this reaction as a preliminary to further studies. In spite of the limitations in using experimental Arrhenius parameters, the value of these, nevertheless, provides us with a convenient criterion for comparisons, though, as will be noticed further in this note, this is not always feasible. Both activation energies and frequency factors may be modified by dielectric constant as well as the viscosity of the solvent. Further, very often, the two parameters show changes in the same direction and no single physical property can be expected to show any proper correlation in the case of pure solvents. The use of solvent mixtures enables attention being directed to one physical constant while all others are kept invariant or nearly so. This has been attempted in Parts I, IV and V (*loc. cit.*).

In all our previous reports, the results presented related to solvents of constant composition, primarily because of the ease of preparing these solvent mixtures. Where polar solvents are involved, as has invariably been the case, both dielectric constant and viscosity change with temperature and for comparisons in a 'constant' electrical environment, a better choice is to consider rate constant under iso-dielectric conditions. As an approximation, this may be done by graphical interpolation of our earlier data. The results of such interpolation is presented in Table I.

The inadequacy of dielectric constant as a criterion for distinguishing between ion dipole and dipole-dipole reactions was noticed in the earlier parts, where deviations from the two accepted correlations for such reactions were noticed. The position is shown in still greater relief by comparing the iso-dielectric rate constants presented here. Even using only the narrow range from dielectric constant 75 to 45, the abnormalities

TABLE I. *Acid Hydrolysis of Ethyl Acetate*
First Order Rate Constants in Iso-dielectric Solvent Mixtures

Dielectric constant	T: 35° C. $k_1 \times 10^4$	45° C. $k_1 \times 10^4$	50° C. $k_1 \times 10^4$
	A. Dioxan-Water system		
74·93	2·806	6·35	14·0
66·13	2·625	6·30	13·7
57·32	2·582	6·05	13·3
40·67	2·163	5·06	11·7
24·82	1·614	3·97	8·77
10·34	1·096	2·77	6·12
5·40	1·147	3·33	6·38
	B. Acetone-Water system		
70·63	2·587	6·27	13·85
66·17	2·331	5·75	12·92
56·29	1·817	4·46	10·00
44·99	1·367	3·12	7·00
32·12	0·937	2·30	5·00
25·22	0·965	2·35	5·17

C. Glycerol-Water system

Dielectric constant	T: 35° C. $k_1 \times 10^4$	42° C. $k_1 \times 10^4$	50° C. $k_1 \times 10^4$	60° C. $k_1 \times 10^4$
69·60	2·557	3·09	8·400	14·40
63·50	2·945	5·41	9·13	17·59
57·20	3·226	6·20	10·25	23·05
48·20	2·581	5·10	10·50	20·70

are well brought by comparing the rates at the two temperatures common to the three solvent mixtures. This is shown in Figs. 1 and 2 below.

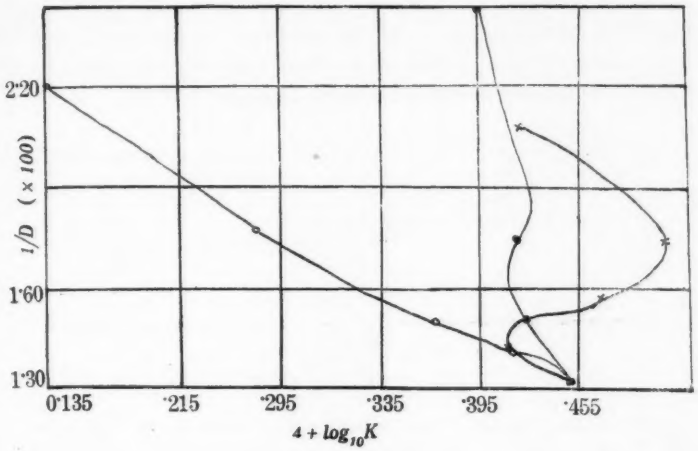

FIG. 1. Ordinate 4 plus $\log_{10}$ k. Abscissa $100 \times 1/D$. Points on ordinate, 0·135, 0·215, 0·295, 0·335, 0·395, 0·435. Points on abscissa, 1·30, 1·60, 1·90, 2·20.

x = Glycerol-water. ● = Dioxan-water. o = Acetone-water.

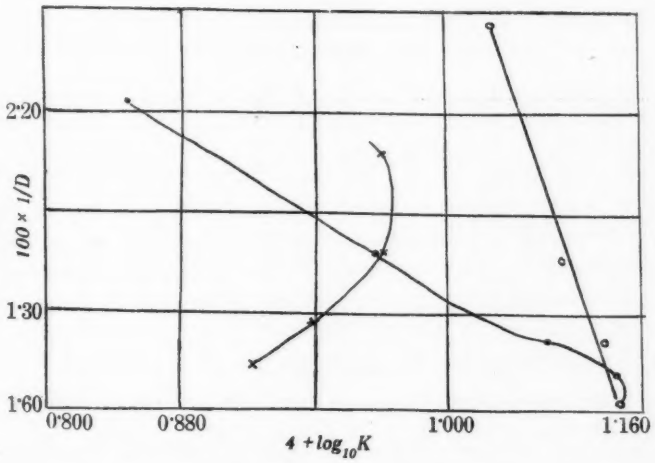

FIG. 2. Co-ordinates and points as in Fig. 1. Figures on Ordinate, 0·800, 0·880, 0·940. 2·000, 1·160. Abscissa as in Fig. 1.

In the case of isocomposition mixtures, a strict linearity between logarithm of rate constant and reciprocal of temperature was observed so that the two Arrhenius parameters could be calculated. The change to iso-dielectric conditions, however, gives us curves which show considerable deviations from linearity, which can be attributed to various causes, some of which are considered later in this note. It is none the less useful to compare the curves and these are presented in Figs. 3, 4 and 5 below.

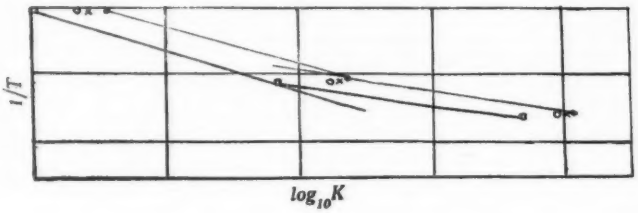

FIG. 3

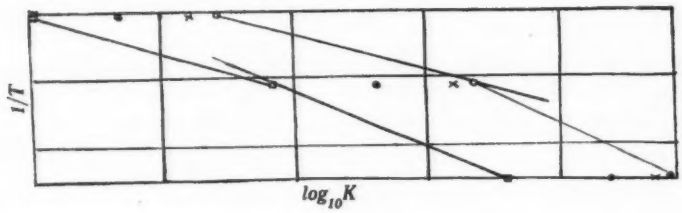

FIG. 4

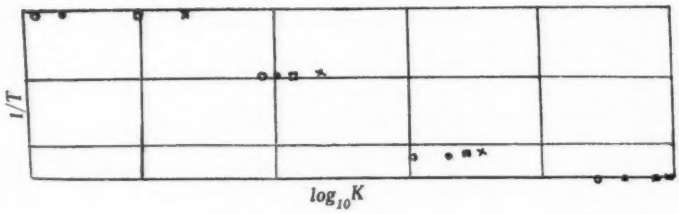

FIG. 5

FIGS. 3, 4 and 5. Abscissa 1/T, Ordinate $\log_{10}$ k.

FIG. 3. Dioxan-water; FIG. 4. Acetone-water; FIG. 5. Glycerol-water.

We may now turn our attention to alkaline hydrolysis in mixed solvents. Rate constants for iso-dielectric conditions may be obtained by analogous methods. The results are collected in Table II.

TABLE II. *Iso-dielectric Second Order Rate Constants in Alkaline Hydrolysis of Ethyl Acetate in Mixed Solvents*

Dielectric constant	k_2 at 30° C. $\times 10^5$	k_2 at 40° C. $\times 10^3$
A. Dioxan-Water system		
76·8 (water)	1·62	2·80
67·75	1·67	2·88
58·80	1·28	2·67
50·43	1·12	2·32
41·80	1·01	1·95
33·51	0·86	1·64
25·53	0·74	1·41
B. Acetone-Water system		
72·31	1·55	2·85
67·75	1·40	2·87
62·70	1·15	2·30
57·60	0·98	1·96
51·98	0·80	1·48
39·53	0·65	1·11

As with acid hydrolysis, here also, no clear correlation between dielectric constant and rate constant is found and we have the same abnormality on the initial addition of the organic solvent to water.

It is recognised that the reactivity of a compound is influenced by the state of polarisation as well as the polarisability of the bond which is primarily involved in the change. The former is essentially a constant while polarisability is liable to changes in the environment. In an earlier communication,[1] it has been shown that there is a close correlation between the characteristic frequency and the logarithm of rate constant and the analysis showed that in ester hydrolysis, one has to consider the carbon-oxygen bond polarisability. If changes in solvent composition alter this one may expect a change in the frequency with change in solvent. No data are, however, available to test this. Some information may be expected by a slightly different approach.

Ingold and coworkers[4] have shown from a study of the rate constants of acid and alkaline hydrolysis of a series of aromatic esters that there is a close correlation between the ratio of the two rate constants and the dipole

moment of the compound. In our present study, using only a single ester namely, ethyl acetate, no change in dipole moment is to be expected but changes in polarisation are not ruled out. A comparison of the two rate constants may thus be expected to give us useful information. So long as we restrict comparison to values at the same temperature, experimental values can be directly used. In the case of acid hydrolysis, these values have to be computed from the known temperature relationships in solvents of constant composition and to this extent the results are only approximate. The values obtained are given in Table III.

TABLE III. *Ratio of the Rate Constants of Alkaline and Acid Hydrolysis of Ethyl Acetate in Solvents of Different Composition*

% Organic solvent in mixture	30° C.		40° C.	
	Dioxan-Water	Acetone-Water	Dioxan-Water	Acetone-Water
0	810		910	
10	670	800	730	980
20	690	800	800	900
30	490	1,725	815	850
40	670	935	810	1,000
50	1,075	1,170	1,280	1,325
60	825	910	980	925

At neither of the temperatures can a definite trend be indicated for either solvent. Generally, the ratios in the case of acetone-water tends to be higher than those of dioxan-water and at higher temperatures, the two ratios approach each other.

Several causes may contribute to the observed variations. The activity of the hydrogen and hydroxyl ions may not be the same in the different solvents. The reactant is essentially a solvated proton in acid hydrolysis and the dimensions of this solvated ion will depend on which solvent is associated with the ion during the reaction. The frequency factor which is governed by the dimensions of the ion as well as the viscosity of the solvent will show changes under these conditions. But these cannot account for the extent of change and apparent vagaries obvious from the tables. The most significant factor is likely to be the environment of the reactant molecules.

While the hydronium ion and possibly even the ethyl acetate molecule may be considered approximately spherical, the hydrogen ion solvated by

acetone or dioxan molecules will have different shapes and conditions analogous to those of anisotropic liquids can arise locally. A proper analysis of the reaction requires a knowledge of the potential ϕ in the environment, which in its turn is related to the total polarisation. It is not feasible to calculate this at present for mixed solvents. Variations have to be expected with composition arising from two principal causes. As a consequence of interionic attraction, one has to expect the polarised ester molecule to be surrounded by an atmosphere of solvated ions. While the larger dimensions of the organic solvents facilitate a certain amount of close packing, the hydronium ion will have to be differently distributed. At lower temperatures this structural factor is not negligible while a rise in temperature minimises the influence. Consequently, at higher temperatures, the ratio of the rate constants of acid and alkaline hydrolysis approaches the same value in corresponding solvent compositions. A fuller understanding is possible only after further work with variations in all the parameters involved and with a larger number of esters.

Summary

The data obtained in earlier work have been recalculated to give the rate constants under iso-dielectric conditions. These results clearly show that specific solvent effects are present in both acid and alkaline hydrolysis. There is a possible change in the polarisation of the ester molecule with composition in which structural changes in the liquid state presumably play a part.

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CERTAIN TRIGONOMETRIC SUMMATIONS

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The trigonometric series considered below have been encountered in the course of certain investigations in room-acoustics and in view of the occurrence of similar series in diverse physical problems, we consider it of some interest to present here an elementary method of expressing them in terms of standard functions. Using these transformations, it is shown that some results due to Krishnan[1] and Goddard[2] are derivable.

We consider the trigonometric series

$$\sum_{n=1}^{\infty} \frac{\sin(n+\theta)x}{(n+\theta)} \cdot \frac{\sin(n+\phi)x}{(n+\phi)}, \quad 0 < x < \pi \tag{1}$$

and the corresponding series in cosines

$$\sum_{n=1}^{\infty} \frac{\cos(n+\theta)x}{(n+\theta)} \cdot \frac{\cos(n+\phi)x}{(n+\phi)}, \quad 0 < x < \pi \tag{2}$$

which are denoted here by $A(\theta, \phi; x)$ and $B(\theta, \phi; x)$ respectively.

We use the following known results[3]

(A) $$c(\theta, x) = \sum_{n=1}^{\infty} \frac{\cos(n+\theta)x}{(n+\theta)}$$

$$= \tfrac{1}{2} \int_x^{\pi} \frac{\cos(\theta - \tfrac{1}{2})t}{\sin \tfrac{1}{2}t}\, dt + \tfrac{1}{2}\left[\psi\left(\frac{1+\theta}{2}\right) - \psi\left(\frac{\theta}{2}\right)\right] \cos \pi\theta - \frac{\cos \theta x}{\theta}$$

(B) $$s(\theta, x) = \sum_{n=1}^{\infty} \frac{\sin(n+\theta)x}{(n+\theta)}$$

$$= \tfrac{1}{2} \int_x^{\pi} \frac{\sin(\theta - \tfrac{1}{2})t}{\sin \tfrac{1}{2}t}\, dt + \tfrac{1}{2}\left[\psi\left(\frac{1+\theta}{2}\right) - \psi\left(\frac{\theta}{2}\right)\right] \sin \pi\theta - \frac{\sin \theta x}{\theta}$$

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where

$$\psi(z) = \frac{\Gamma'(z)}{\Gamma(z)} = \operatorname*{Lim}_{n\to\infty}\left[\log n - \frac{1}{z} - \frac{1}{1+z} - \frac{1}{2+z} - \ldots - \frac{1}{n+z}\right].$$

The series (1) can now be transformed thus

$$\begin{aligned} A(\theta, \phi;\ x) &= \tfrac{1}{2}\sum_{n=1}^{\infty}\frac{\cos(\theta-\phi)x - \cos[n+\tfrac{1}{2}(\theta+\phi)]\,2x}{(n+\theta)(n+\phi)} \\ &= \tfrac{1}{2}\frac{\cos(\theta-\phi)\,x}{(\theta-\phi)}\sum_{n=1}^{\infty}\left(\frac{1}{n+\phi} - \frac{1}{n+\theta}\right) \\ &\quad + \tfrac{1}{2}\frac{1}{\theta-\phi}\sum_{n=1}^{\infty}\left(\frac{1}{n+\theta} - \frac{1}{n+\phi}\right)\cos[n+\tfrac{1}{2}(\theta+\phi)]\,2x \end{aligned}$$

Writing the terms $\dfrac{\cos[n+\frac{1}{2}(\theta+\phi)]\,2x}{n+\theta}$ and $\dfrac{\cos[n+\frac{1}{2}(\theta+\phi)]\,2x}{n+\phi}$ as

$\dfrac{\cos[n+\theta-\frac{1}{2}(\theta-\phi)]\,2x}{n+\theta}$ and $\dfrac{\cos[n+\phi+\frac{1}{2}(\theta-\phi)]2x}{n+\phi}$ respectively,

$A(\theta, \phi;\ x)$ can be transformed as

$$\begin{aligned} A(\theta, \phi;\ x) &= \tfrac{1}{2}\frac{\cos(\theta-\phi)\,x}{\theta-\phi}[\psi(1+\theta) - \psi(1+\phi)] \\ &\quad + \tfrac{1}{2}\frac{\cos(\theta-\phi)\,x}{\theta-\phi}[c(\theta, 2x) - c(\phi, 2x)] \\ &\quad + \tfrac{1}{2}\frac{\sin(\theta-\phi)\,x}{\theta-\phi}[s(\theta, 2x) + s(\phi, 2x)] \qquad (3) \end{aligned}$$

The series (2) can be written as

$$\begin{aligned} B(\theta, \phi;\ x) &= \sum_{n=1}^{\infty}\frac{\cos(\theta-\phi)\,x - \sin(n+\theta)\,x\sin(n+\phi)\,x}{(n+\theta)(n+\phi)} \\ &= \cos(\theta-\phi)\,x\sum_{n=1}^{\infty}\frac{1}{(n+\theta)(n+\phi)} - A(\theta, \phi;\ x) \end{aligned}$$

so that we have finally

$$\begin{aligned} B(\theta, \phi;\ x) &= \tfrac{1}{2}\frac{\cos(\theta-\phi)\,x}{\theta-\phi}[\psi(1+\theta) - \psi(1+\phi)] \\ &\quad - \tfrac{1}{2}\frac{\cos(\theta-\phi)\,x}{\theta-\phi}[c(\theta, 2x) - c(\phi, 2x)] \\ &\quad - \tfrac{1}{2}\frac{\sin(\theta-\phi)\,x}{\theta-\phi}[(s(\theta, 2x) + s(\phi, 2x)] \qquad (4) \end{aligned}$$

When $\theta = \phi$, $A(\theta, \theta;\ x)$ and $B(\theta, \theta;\ x)$ are easily obtained from (3) and (4) by passing to the limit. Then

$$A(\theta, \theta; x) = \tfrac{1}{2}\frac{d\psi(1+\theta)}{d\theta} + \tfrac{1}{2}\frac{dc(\theta, 2x)}{d\theta} + xs(\theta, 2x) \quad (3)$$

$$B(\theta, \theta; x) = \tfrac{1}{2}\frac{d\psi(1+\theta)}{d\theta} - \tfrac{1}{2}\frac{dc(\theta, 2x)}{d\theta} - xs(\theta, 2x) \quad (4)$$

We now derive certain trigonometric summations:

I. The transformation (3) can be used to obtain the elegent summation*

$$\sum_{n=1}^{\infty}\left[\frac{\sin(n-\theta)x}{n-\theta} - \frac{\sin(n+\theta)x}{n+\theta}\right]\left[\frac{\sin(n-\phi)x}{n-\phi} - \frac{\sin(n+\phi)x}{n+\phi}\right]$$
$$= \pi\left[\frac{\sin(\theta-\phi)x}{\theta-\phi} - \frac{\sin(\theta-\phi)x}{\theta-\phi}\right] \quad (5)$$

II. Adding $A(\theta, \theta; x)$ and $A(-\theta, -\theta; x)$ we obtain

$$\sum_{n=1}^{\infty}\frac{\sin^2(nx+\alpha)}{(nx+\alpha)^2} = \frac{\pi}{x}, \quad (6)$$

where $\alpha = \theta x$, a result used by Krishnan in Light Scattering (*loc. cit.*).

III. Taking $\phi = -\theta$ in (3) we get

$$\sum_{n=1}^{\infty}\frac{\sin(n+\theta)x\sin(n-\theta)x}{n^2-\theta^2} = \frac{\sin^2\theta x}{2\theta^2} + \frac{\pi}{4}\frac{\sin 2\theta x}{\theta}.$$

In particular, when $\theta = \alpha m$ and $x = \pi/\alpha$, where α is real and > 1, and m is a positive integer, the above relation becomes

$$\sum_{n=1}^{\infty}\frac{\sin^2(n\pi/\alpha)}{n^2-\alpha^2m^2} = 0 \quad (8)$$

a result used by Goddard (*loc. cit.*),

IV. By employing the transformation (4) we can obtain the following summation analogous to (5)

$$\sum_{n=1}^{\infty}\left[\frac{\cos(n-\theta)x}{n-\theta} - \frac{\cos(n+\theta)x}{n+\theta}\right]\left[\frac{\cos(n-\phi)x}{n-\phi} - \frac{\cos(n+\phi)x}{n+\phi}\right]$$
$$= \tfrac{1}{2}\left(\frac{1}{\theta} - \pi\cot\pi\theta\right)\left[\frac{\cos(\theta-\phi)x}{\theta-\phi} - \frac{\cos(\theta+\phi)x}{\theta+\phi}\right]$$
$$- \tfrac{1}{2}\left(\frac{1}{\phi} - \pi\cot\pi\phi\right)\left[\frac{\cos(\theta-\phi)x}{\theta-\phi} + \frac{\cos(\theta+\phi)x}{\theta+\phi}\right]$$
$$- \left[\frac{\sin(\theta-\phi)x}{\theta-\phi} - \frac{\sin(\theta+\phi)x}{\theta+\phi}\right] \quad (9)$$

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   See Bromwich, T. J. I'A (McMillan, 1926).

*It was necessary to sum this particular series in our problem referred to.

PARAMAGNETIC RESONANCE IN SOME CUPRIC SALTS

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1. Introduction

By reason of their interesting magnetic properties, the cupric salts have been studied for their paramagnetic resonance spectra in some detail by many workers. In fact, of the ions of the iron group of elements, Cu^{++}, with electronic configuration $3d^9$ occurs with spin $S = \frac{1}{2}$ only, when the orbital momentum is quenched and is therefore the simplest. The quenching of the orbital moment takes place in all the salts of copper as revealed by the extensive susceptibility data available. In order to explain the magnetic properties of the cupric salts, the predominance of exchange forces between the ions is invoked in addition to various types of internal electric fields which contribute to the quenching of the orbital moment. The general character of the results show that these two effects predominate but a quantitative understanding of the many interesting features exhibited by the cupric salts await the collection of more data. The study of the paramagnetic resonance spectra of the salts of copper affords a better understanding of the nature of magnetic and electrical interactions in crystals. In the present work the study has been extended to eleven more cupric salts.

2. Experimental

The experimental set up used in the present study is of the conventional type. It consisted of a 3 cm. Klystron (723 A/B) operated from batteries to ensure high stability of the output. Power from the Klystron was fed by means of a long wave-guide to a cavity resonator, resonating in the H_1 mode, between the polepieces of an electromagnet. The electromagnet was capable of maintaining a field of 4,500 oersteds in a gap of $1\frac{1}{4}''$ and cross-section $3''$ square. The output of the cavity resonator was fed to a 1 N 23 crystal rectifier and the rectified current was measured by means of a galvanometer. The galvanometer deflections were reduced to absorption in arbitrary units by means of the familiar formula

$$\sqrt{\frac{\delta_0}{\delta}} - 1 = \text{absorption},$$

where δ_0 is the deflection of the galvanometer when the cavity is tuned to resonance and the magnetic field is far higher than the resonance value. δ is the deflection at any particular magnetic field at which it is desired to know the relative paramagnetic absorption. The magnetic field was found by using manganous salts whose g values are very close to that of a free electron. In the case of single crystals, the crystals were mounted on the lower choke of the cavity, the choke being capable of rotation about the cavity axis through known angles. In the case of deliquescent crystals it is necessary to imbed the crystals in paraffin wax after proper desiccation, because even small amounts of water will lower the cavity Q enormously. Paraffin wax has low loss at these frequencies and the dielectric constant is also not large and it has a low melting point. Hence it is highly suitable for imbedding the crystals when necessary.

3. SUBSTANCES INVESTIGATED

Paramagnetic resonance was sought in the following cupric salts, cupric nitrate, cupric ammino-nitrate, cupric ammonium chloride, basic fluoride of copper, cupric acetate, azurite, cupric carbonate, cupric cyanide and cupric oxide.

TABLE I

Substance	g.	$\Delta H_{\frac{1}{2}}$	$[\Delta H^2]^{\frac{1}{2}}_{AV}$	$[\Delta H^4]^{\frac{1}{4}}_{AV}$	Ratio	Remarks
Cupric ammonium chloride	2·25		220	290	1·38	Anisotropy measurements in single crystals have been made
Cupric nitrate	2·2	390	215	383	1·78	Slight asymmetry in absorption
Cupric ammino nitrate	2·1	320	215	303	1·41	Anisotropy measurements also made
Cupric fluoride, basic	2·08	410	215	370	1·71	Asymmetric absorption
Cupric acetate azurite Cupric carbonate Cupric phosphate Cupric arsenate Cupric cyanide Cupric oxide	Do not show any absorption in the magnetic field range 0–4500 oersteds					

Of these the acetate, azurite, carbonate, phosphate, arsenate, cyanide and oxide did not show any paramagnetic resonance absorption in the range of magnetic fields (0–4,500 oersteds) employed in this investigation. The other compounds showed easily detectable adsorption. The g values, root mean square moment, fourth root of mean fourth moment, their ratios and half-breadths are given in Table I. Only fairly narrow lines are found and it is usual to ascribe the effect to the influence of exchange interaction. The basic fluoride and the nitrate show asymmetric absorption peaks. Another smaller line seems to occur on the lower magnetic field side of the main resonance peak, in these substances. However, it must be remembered that most paramagnetic resonance curves are not truly symmetrical. There is always a small amount of absorption persisting even far below resonance some times up to zero field. This is perhaps due to some non-resonant process. As remarked later, only the data pertaining to the high magnetic field side of the resonance were used in calculating the second and fourth moments. In the case of the acetate, Gordy and Lancaster (1951), Bleaney and Bowers (1951) have reported a field dependent g value and structure of the resonance spectrum by working at frequencies up to 50,000 Mc/s. The case of the oxide seemed of interest at first as the first sample used showed broad resonance effects like those of some antiferromagnetic substances. However, other samples from various sources and degrees of purity were tried but they failed to show any noticeable effect. The nature of the impurity in the first case is not known. As already remarked, the basic fluoride exhibits some structure in its resonance line. The curve for the basic fluoride is given in Fig. 1.

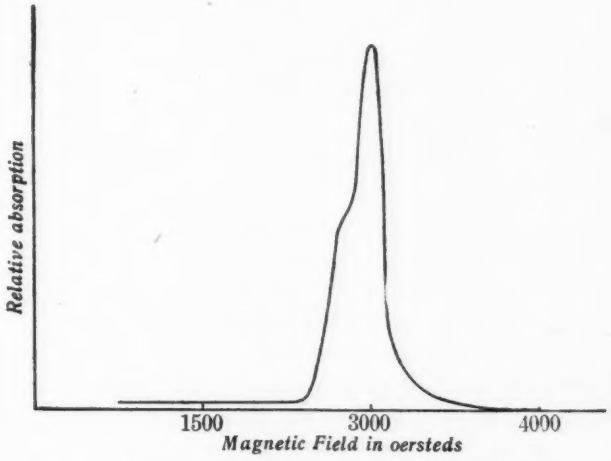

FIG. 1. Resonance curve for the Basic fluoride of Copper

4. ANISOTROPY OF *g* FACTOR AND LINE SHAPE

Single crystals of cupric ammonium chloride and cupric ammino-nitrate were studied in different orientations. Like other similar salts, these also show variation in *g* factor and line shape with orientation. The results are presented in Table II and Fig. 2 for line shape parameters and *g* factor respectively. In calculating the line shape parameters $[\Delta H^2]^{\frac{1}{2}}_{Av}$ and $[\Delta H^4]^{\frac{1}{4}}_{Av}$ the data pertaining to the higher magnetic field side of the resonance curve was alone used on the assumption that side of the

TABLE II

Anisotropy data on $CuCl_2\ 2\ NH_4Cl$:—c-axis lying perpendicular to the cavity axis

Angle	$[\Delta H^2]^{\frac{1}{2}}_{Av}$	$[\Delta H^4]^{\frac{1}{4}}_{Av}$	Ratio	g.
0° ..	220	290	1·38	2·44
30° ..	174	250	1·48	2·40
60° ..	202	246	1·22	2·34
90° ..	147	179	1·22	2·30
120° ..	125	198	1·59	2·33
150° ..	215	280	1·34	2·38
180° ..	128	188	1·43	2·40

resonance curve will be free of complicating factors due to non-resonant absorption and structure due to unresolved lines. The lower side will contribute very much more particularly to the value of the fourth moment as the absorption might sometimes extend upto zero field. Of the copper compounds the chlorides are of interest because the chlorine atoms with their low energy *d* orbitals give scope for the exchange effects to predominate. The data for cupric ammonium chloride are given in curve (*a*) (Fig. 2) and in Table II. The variations with orientation when the crystal is rotated in the *a-c* plane are pronounced and a minimum exists at 120°. This line is very sharp and the exchange interaction seems to contribute a large amount to the fourth moment, whereas at neighbouring angles the line is quite broad and seems to be gaussian. This may be due to anisotropy of exchange interaction. Similar data are reported for the case of copper ammonium selenate by Bleaney, Penrose and Plumpton (1949). About other directions the anisotropy is not marked and the resonance lines are comparatively

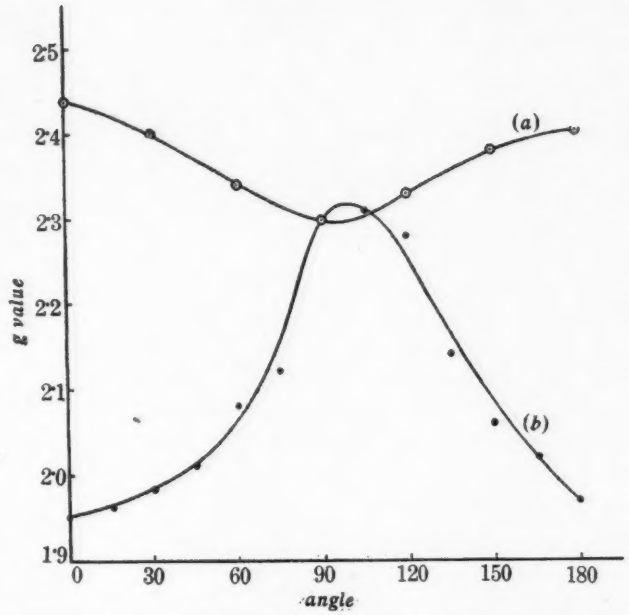

FIG. 2. (*a*) Variation of *g* factor with orientation for cupric ammonium chloride.
(*b*) Variation of *g* factor with orientation for cupric ammino nitrate.

weak and broad. In these directions the *g* value is about 2·3. Some measurements on the potassium and ammonium chlorides of copper have been reported by Fujimoto and Itoh (1951) working in the 3,000 MC region. The *g* values given by them for the potassium salt range from 2·06 to 2·18. A *g* value determination in the case of powdered cupric ammonium chloride has been made by Gordy and Lancaster (1951) and their value is 2·21. The values in the present determination lie mostly about 2·2 to 2·3 but with 2·44 in some directions. The *g* values are thus higher in the ammonium than in the potassium salt.

Cupric ammino-nitrate (monoclinic, prism about *c*-axis) was also investigated for anisotropy about three directions. It was found that sharp resonances could be obtained when the long or the *c*-axis of the crystal was along the magnetic field and the resonance became broader and weaker as the crystal was turned away from this position. The *g* value also varied with direction and the variation is presented in curve (*b*) in Fig. 2. When the crystal was mounted with the *c*-axis vertical, the resonances were weak and there was no variation in the *g* value. The *g* value in this case was found

to be 2·1 as contrasted with values ranging from 1·9 to 2·1 about a direction perpendicular to the planes containing the *c*-axis.

Several substances do not show paramagnetic resonance. One of the objects of this investigation was to find whether there was any compound intermediate between those which show paramagnetic resonance strongly and those which do not show any at all. None of the substances falls into this category. The following may be the reasons for the unobservability of the effect.

1. Relaxation times are too small or too large.

2. Magnetic interaction is very large so that the line is spread out.

3. Sufficiently low energy paths are not available for the electrons to contribute effectively to exchange interactions leading to sharpening of the resonance. It is difficult to say which or what combination of these operate in any particular instance. So further investigations of these salts at low temperatures are needed.

We wish to record our gratitude to Professor R. S. Krishnan for his kind interest and encouragement.

5. SUMMARY

Paramagnetic resonance absorption of 3 cm. wave in eleven copper salts has been studied. Of these four show paramagnetic absorption; *g* factors and half-widths obtained are given. Single crystals of cupric ammonium chloride and cupric ammino-nitrate have been studied for anisotropy in *g* factor and line-shape parameters. Results regarding cupric ammonium chloride indicate that exchange interaction may not be isotropic.

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NUCLEAR OXIDATION IN FLAVONES AND RELATED COMPOUNDS

Part XL. A Study of Morin and Datiscetin Derivatives

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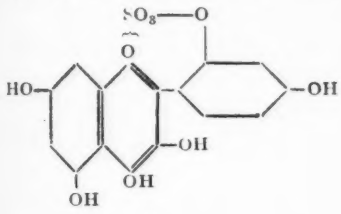
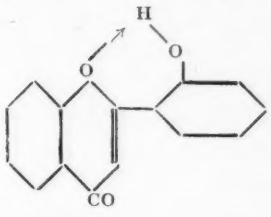
Received June 4, 1952

In anthoxanthins the presence of a hydroxyl group in the 2′-position is somewhat unusual. Among naturally occurring flavonols, morin and datiscetin have this characteristic. A 2′-hydroxyl group appeared to have some influence on the properties of these compounds. The earliest record is the peculiar formation and composition of morin sulphate (I) by Robinson and Venkataraman.[1] Other observations have been made more recently in this laboratory in the case of related groups, *e.g.*, flavanones[8]. The results of experiments made with flavonols of this type are related in this paper.



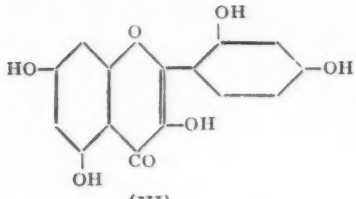
(I)



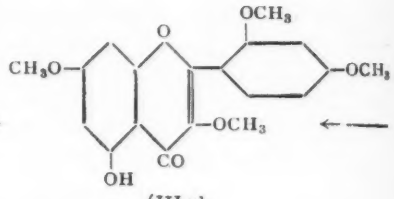
(II)

The possibility of chelation (II) involving the 2′-hydroxyl group and the pyrone oxygen atom and the consequent resistance of this hydroxyl to methylation seemed to require consideration. That an ether oxygen atom can form hydrogen bonds with facility has been shown in the study of these bonds by the use of the Raman effect.[2] As could be seen from the formula (II) the chelate ring would contain six atoms and hence may be expected to be stable. Experiments have therefore been conducted using morin, datiscetin and their derivatives for obtaining their partial methyl ethers. With three and four moles of dimethyl sulphate, morin (III) yields the same 3: 7: 2′: 4′-tetramethyl ether (III *a*), although the yield is lower in the first case, showing that there is no particular resistance to the methylation of the 2′-hydroxyl group. The same tetramethyl ether is also obtained by methylation with one mole of dimethyl sulphate of the synthetic 3: 2′- 4′-trimethyl

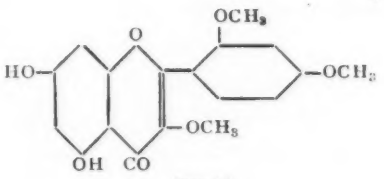
ether of morin (III *b*). This proves that the hydroxyl group left out is in the 5th position and not in 2′. Excess of dimethyl sulphate and potassium carbonate in acetone medium yield O-pentamethyl-morin and this procedure is far more convenient for preparing this substance than earlier methods. Resomorin (IV *a*) and resodatiscetin (7 : 2′-dihydroxy-flavonol) (IV *b*) do not undergo partial methylation and all the hydroxyl groups are easily attacked, thus confirming that there is no particular resistance to methylation offered by the 2′-hydroxyl group. These results would indicate that chelation involving the 2′-hydroxyl group is not present to any marked extent in the case of flavonols.



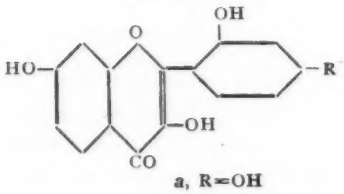
(III)



(III *a*)



(III *b*)

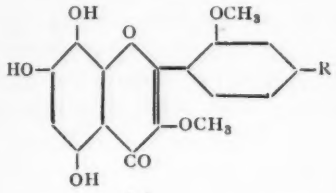


a, R=OH
b, R=H

(IV)

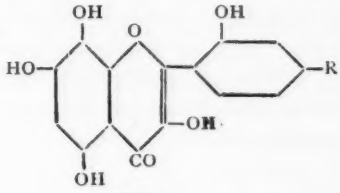
Just as in the case of other flavonols, having the 5 : 7-hydroxyl groups, nuclear oxidation of morin and datiscetin may also occur in nature giving rise to 8-hydroxy derivatives. Though they have not been isolated from natural sources so far, possibility of their existence should be accepted. Hence persulphate oxidation has been carried out using partial methyl ethers of morin (III *b*) and datiscetin which are readily obtained by syntheses. The oxidation takes place readily giving rise in good yields to the 8-hydroxy compounds (V *a*) and (V *b*). These give all the characteristic

reactions for the presence of the 5:7:8-hydroxy grouping. Complete methylation has subsequently been carried out, and also demethylation to the fully hydroxylated compounds (VI *a* and *b*). No isomeric change is found to take place in the demethylation and the products are found to have all the properties of 5:7:8-trihydroxy compounds. This has been confirmed by remethylation in the case of 8-hydroxy datiscetin to 3:5:7:8:2′-pentamethoxy flavone and is in agreement with the behaviour under hydriodic acid demethylation of other flavonol derivatives in which the presence of the 3-hydroxyl group prevents the isomeric change.[3]



(V)

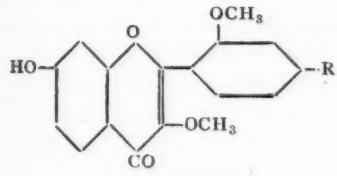
a, R=OCH_3
b, R=H



(VI)

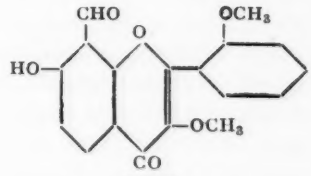
a, R=OH
b, R=H

As an example of ortho-oxidation the preparation of 8-hydroxy-resodatiscetin (IX *b*) has been carried out. The partial methyl ether of resodatiscetin (VII *b*) readily forms the 8-aldehyde (VIII), which can be oxidised by alkaline hydrogen peroxide to yield the corresponding 8-hydroxy compound (IX *a*).

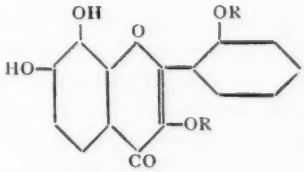


(VII)

a, R=OCH_3
b, R=H



(VIII)



(IX)

a, R=CH_3
b, R=H

EXPERIMENTAL

O-3 : 2′ : 4′-*Trimethylmorin* (*III b*).—

It was prepared according to the method adopted by Robinson and Venkataraman.[1] But O-dimethyl-β-resorcylic acid required for this purpose was made by the methylation of β-resorcylic acid using excess of dimethyl sulphate and anhydrous potassium carbonate in dry acetone solution. The crude ether ester first obtained was directly hydrolysed to yield the required acid. The O-trimethylmorin (III *b*) is found to melt at 231–2° instead of at the earlier recorded melting point of 132° which is definitely too low for a substance of this constitution. All other properties agree (Found: C, 62·9; H, 5·0; $C_{18}H_{16}O_7$ requires C, 62·8; H, 4·7%). Its diacetyl derivative obtained by refluxing it with acetic anhydride and a few drops of pyridine for six hours, crystallised from aqueous alcohol as small rectangular prisms melting at 161–2°.

O-3 : 7 : 2′ : 4′-*Tetramethylmorin* (*III a*) *and O-pentamethyl morin*

A solution of morin trimethyl ether (III *b*) (0·58 g.) in dry acetone (100 c.c.) was refluxed with dimethyl sulphate (0·2 c.c., 1 mole) and anhydrous potassium carbonate (1 g.) for sixteen hours. Acetone was distilled off and water added to the residue. The mixture was extracted with ether and the ether solution repeatedly extracted with aqueous alkali. The alkaline solution was acidified when a colourless crystalline solid separated out. It was filtered, washed with water and crystallised from alcohol when it was obtained as elongated prisms and rods melting at 132–3°. Yield, 0·5 g. With alcoholic ferric chloride, it gave a violet colour turning olive brown. Its yellow solution in concentrated sulphuric acid exhibited light green fluorescence. It dissolved in 5% aqueous sodium hydroxide to a yellow solution. On acetylation with acetic anhydride in presence of pyridine it gave the mono-acetyl derivative which crystallised from aqueous alcohol as colourless rectangular prisms melting at 168°. The melting points of tetramethyl ether and its acetyl derivative agree with those recorded in the literature.[4]

A mixture of O-trimethyl-morin (III *b*) (0·5 g.), dry acetone (100 c.c.), dimethyl sulphate (0·8 c.c., excess) and freshly ignited potassium carbonate (2 g.) was refluxed till the solution did not give any colour with alcoholic ferric chloride (30 hours). The potassium salts were then separated by filtration, washed with warm acetone and the filtrate was distilled to remove acetone. On adding petroleum-ether to the residue, the pentamethyl ether separated as a colourless crystalline solid which crystallised from alcohol as colourless clusters of needles melting at 155–6°, and agreeing with the melting point recorded in the literature.[1, 5]

Methylation of morin (III)

Morin was obtained by the demethylation of morin trimethyl ether (III *b*) with hydriodic acid, following the procedure of Robinson and Venkataraman.[1] It could be conveniently crystallised from aqueous pyridine when it was obtained as tiny yellow needles melting at 286–9° with sintering at 280°.

(*a*) A solution of morin (III) (0·5 g.) in 150 c.c. of dry acetone was treated with freshly distilled dimethyl sulphate (0·55 c.c.; 3 moles) and freshly ignited potassium carbonate (2 g.) and refluxed on a water-bath under dry conditions for 24 hours. The acetone solution was filtered and the potassium salts were washed well with warm dry acetone. Acetone was then removed from the filtrate and the residue crystallised from dilute alcohol when it separated as elongated rectangular prisms and rods melting at 132–3°. Yield, 0·3 g. With alcoholic ferric chloride it gave a reddish violet colour immediately turning olive brown and dissolved in aqueous sodium hydroxide to a yellow solution. The acetyl derivative made from it as usual melted at 168°. Mixed melting points of this methyl ether and its acetyl derivative with authentic samples of O-2′: 4′: 3: 7-tetramethyl-morin (III *a*) and its acetate respectively showed no depression.

(*b*) When the methylation of morin (III) (0·5 g.) was repeated using 4 moles of dimethyl sulphate, the product was found to melt at 132–3° and also the colour reactions and its acetyl derivative were identical with those of O-3: 7: 2′: 4′-tetramethyl morin (III *a*). Yield, 0·48 g.

(*c*) Morin (0·5 g.) together with acetone (80 c.c.), anhydrous potassium carbonate (6 g.) and dimethyl sulphate (1·5 c.c.; over 5 moles) was refluxed until it gave no colour with alcoholic ferric chloride (40 hours). The product crystallised from alcohol as clusters of colourless needles melting at 155–6°. Yield, 0·5 g. It was found to be identical with the O-pentamethyl morin.

O-3: 2′: 4′-*Trimethylresomorin* (*VII a*)

An intimate mixture of ω-methoxy-resacetophenone (3 g.), sodium 2: 4-dimethoxy benzoate (6 g.) and 2: 4-dimethoxy benzoic anhydride (18 g.) was heated at 180–84° for four hours under diminished pressure. After cooling, the product was dissolved in boiling alcohol (120 c.c.); a solution of potassium hydroxide (8 g.) in water (20 c.c.) added and the liquid refluxed for thirty minutes. Alcohol was removed from the mixture by distilling it under reduced pressure and the residue left was dissolved in 500 c.c. of water. The passage of carbon dioxide caused the slow precipitation of a yellow solid which was partly crystalline. The precipitate was dissolved in boiling alcohol (100 c.c.), treated with animal charcoal and filtered. On

cooling, it deposited colourless thin laminæ of resomorin-3 : 2′ : 4′-trimethyl ether melting at 253–55°. Another crop could be obtained by concentrating the mother liquor. Total yield, 4·75 g. It is moderately soluble in most of the organic solvents but is sparingly soluble in ether and petroleum-ether. It dissolves in aqueous alkali to a yellow solution and its yellow solution in concentrated sulphuric acid exhibits light green fluorescence. It does not give any colour with alcoholic ferric chloride and addition of lead acetate to its alcoholic solution gives a yellow precipitate (Found: C, 65·6; H, 5·1; $C_{18}H_{16}O_6$ requires C, 65·8; H, 4·9%).

It was acetylated by boiling it with acetic anhydride and a few drops of pyridine. The product crystallised from ethyl acetate-petroleum ether as narrow rectangular plates and prisms melting at 134–35° (Found: C, 65·3; H, 4·5; $C_{20}H_{18}O_7$ requires C, 65·0; H, 4·8%).

O-*Tetramethylresomorin*

A solution of the above trimethyl ether (VII *a*) (320 mg.) in acetone (40 c.c.) was refluxed for 8 hours with dimethyl sulphate (0·2 c.c.) and potassium carbonate (1 g.). The product crystallised from alcohol in the form of colourless stout triangular prisms melting at 155–6°; yield, 300 mg. (Found: C, 66·9; H, 5·5; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%).

Resomorin (*IV a*)

Resomorin trimethyl ether (VII *a*) (1 g.) was dissolved in acetic anhydride (8 c.c.) and hydriodic acid (15 c.c.; d, 1·7) was added after cooling the solution in ice. The mixture was refluxed for two hours, poured over ice and saturated with sulphur dioxide to remove iodine present, when a brownish yellow mass separated out. It was collected, washed well with water and crystallised twice from aqueous pyridine when small yellow needles melting at 274–5° were obtained. Yield, 0·5 g. (Found: C, 63·0; H, 3·6; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%). It is moderately soluble in all organic solvents but slightly so in petroleum ether and these solutions give green fluorescence. It gives olive green colour with alcoholic ferric chloride, and yellow solution in concentrated sulphuric acid. It dissolves in aqueous sodium hydroxide and sodium carbonate to a yellow solution exhibiting green fluorescence.

Methylation of resomorin

(*a*) Resomorin (IV *a*) (0·45 g.) was dissolved in acetone (50 c.c.), dimethyl sulphate (0·5 c.c.) and potassium carbonate (2 g.) added and the mixture refluxed for twenty hours. Acetone was distilled off and water added to dissolve potassium salts. The mixture was extracted with ether

and the ether solution extracted repeatedly first with aqueous sodium carbonate and then with sodium hydroxide. It was finally washed with water. The sodium hydroxide solution did not give any significant amount of substance on acidification, whereas the carbonate solution yielded unchanged resomorin (0·1 g.). The ether solution on concentration deposited a colourless crystalline solid (0·3 g.) which crystallised from acetone as colourless stout rectangular prisms melting at 155–56°. It neither gave any colour with alcoholic ferric chloride nor any acetyl derivative and did not depress the melting point of resomorin tetramethyl ether.

(*b*) When resomorin (IV *a*) was refluxed in dry acetone solution with dimethyl sulphate (4 moles and excess) and potassium carbonate for 15 hours resomorin-tetramethyl ether was obtained in quantitative yield.

O-3: 2'-*Dimethyl-resodatiscetin* (*VII b*)

An intimate mixture of ω-methoxy resacetophenone (3 g.), sodium 2-methoxy benzoate (4·5 g.) and 2-methoxy benzoic anhydride (12 g.) was heated at 170–80° under reduced pressure for three hours. The product was hydrolysed with alcoholic potash (6 g. in 120 c.c.) and the passage of carbon dioxide in the diluted solution deposited the flavonol as a yellow crystalline solid which crystallised from ethyl acetate-petroleum ether mixture as colourless small needles melting at 244°. Yield, 4·5 g. It gives with magnesium and hydrochloric acid a light orange colour, no colour with alcoholic ferric chloride and yellow solution in concentrated sulphuric acid. It dissolves in aqueous sodium hydroxide and sodium carbonate to a yellow solution (Found: C, 68·3; H, 4·9; $C_{17}H_{14}O_5$ requires C, 68·4; H, 4·7%).

O-*Trimethyl-resodatiscetin*

The above dimethyl ether (VII *b*) was methylated using 1·5 moles of dimethyl sulphate under dry conditions as usual. The trimethyl ether crystallised from methyl acetate as colourless tiny prisms melting at 133–34° (Found: C, 69·0; H, 5·0; $C_{18}H_{16}O_5$ requires C, 69·2; H, 5·1%).

Resodatiscetin (*IV b*)

A mixture of resodatiscetin-dimethyl ether (VII *b*) (0·5 g.), acetic anhydride (10 c.c.) and hydriodic acid (d. 1·7, 10 c.c.) was refluxed for one hour and then poured in a saturated ice-cold solution of sodium bisulphite, when resodatiscetin separated out as a light yellow crystalline solid. It crystallised from ethyl acetate-petroleum ether mixture as aggregates of small colourless rectangular prisms melting at 272–3°. Kostanecki and Szlagier[6] who adopted a different method reported the melting point as 271°.

Methylation of resodatiscetin

It was carried out in the same way as that of resomorin. When three moles or excess of dimethyl sulphate was used, the trimethyl ether (melting point 133–4°) was obtained in quantitative yield. Even with two moles of the reagent, the same trimethyl ether was produced in 60% yield along with unchanged resodatiscetin (40%). This clearly proves that the hydroxyl in the 2′-position is not resistant to methylation.

5: 7: 8-*Trihydroxy*-3: 2′: 4′-*trimethoxy flavone* (*V a*)

To a stirred ice-cold solution of 5: 7-dihydroxy-3: 2′: 4′-trimethoxy flavone (III *b*) (1 g.) in sodium hydroxide (0·5 g. in 50 c.c. of water) was added drop by drop, a solution of sodium persulphate (1·5 g. in 50 c.c. of water) in the course of two hours. After twenty-four hours the solution was neutralised with hydrochloric acid using congo-red as the indicator; the unchanged flavone thus precipitated was filtered off and traces of it present in the solution were removed by extraction with ether. Conc. hydrochloric acid (20 c.c.) and sodium bisulphite (1 g.) were then added to the aqueous solution which was heated for ten minutes at 80° and then left to cool. The oxidation product was obtained as a bright yellow precipitate. It was filtered, washed and dried. It crystallised from ethyl acetate as beautiful yellow clusters of tiny needles melting at 238–9°. Yield, 0·58 g.

5: 7: 8-*Trihydroxy*-3: 2′: 4′-trimethoxy-flavone (V *a*) is moderately soluble in all organic solvents but sparingly soluble in ether and petroleum ether. It dissolves easily in aqueous alkali to give a yellow solution turning green and then bluish green. It dissolves in sodium carbonate with difficulty to give pale yellow solution changing to bright yellow. It gives with alcoholic ferric chloride an olive green colour which rapidly changes to brown. Its yellow solution in sulphuric acid gives no fluorescence. With *p*-benzoquinone it gives reddish brown colour (Found: C, 59·7; H, 4·5; $C_{18}H_{16}O_8$ requires C, 60·0; H, 4·4%).

3: 5: 7: 8: 2′: 4′-*Hexamethoxyflavone*

The above trihydroxy-trimethoxy-flavone (V *a*) (0·5 g.) was methylated by refluxing in dry acetone solution (150 c.c.) with dimethyl sulphate (0·7 c.c.) and anhydrous potassium carbonate (2 g.) for thirty hours. The solution was then filtered off and potassium salts washed well with hot dry acetone. The solvent was then distilled off from the filtrate. The residue crystallised from benzene-petroleum ether (b.p. 55–65°) mixture to give colourless thin plates, melting at 140–1°. Yield, 0·5 g. It is insoluble in alkali, and gives a yellow solution in concentrated sulphuric acid and gives no colour with

alcoholic ferric chloride (Found: C, 62·5; H, 5·5; $C_{21}H_{32}O_8$ requires C, 62·7; H, 5·5%).

3:5:7:8:2′:4′-*Hexa-hydroxy-flavone* (8-*Hydroxy-morin VI a*)

To an ice-cooled solution of 5:7:8-trihydroxy-3:2′:4′-trimethoxy flavone V *a* (0·5 g.) in acetic anhydride (10 c.c.) was slowly added hydriodic acid (15 c.c.; d. 1·7) and then the whole solution was refluxed for an hour. It was observed that longer heating caused the darkening of the resulting product. The solution was poured in an ice-cooled solution of sodium bisulphite to remove iodine when orange yellow flakes of 8-hydroxy-morin separated out. These were collected, washed well with water and dried in a vacuum desiccator. The product offered great difficulties in crystallising and it seemed to be unstable in air and when boiled with organic solvents. This was extracted exhaustively with acetone and the impurities precipitated from this solution by adding ether to it. The clear yellow solution on concentration became dark and nothing crystallised out after keeping it for one day. The solvent was removed and the residue was dissolved in ethyl acetate. Dark impurities were carefully removed from the solution by precipitating them with petroleum-ether. Further addition of more petroleum-ether to the clear yellow solution yielded yellow crystalline solid. It was filtered, washed with petroleum-ether containing a few drops of ethyl acetate. When this solid was seen under the microscope it appeared as small yellow rectangular plates and prisms, m.p. 295–98°. Yield, 50 mg. (Found: C, 51·2; H, 4·6; $C_{15}H_{10}O_8$, 2 H_2O requires C, 50·9; H, 3·9%).

It dissolves in aqueous saturated sodium bicarbonate solution giving a yellow colour which immediately turns brown and after half a minute a stable brown pink solution results. Its solution in aqueous sodium carbonate assumes successively yellow, brown, olive brown and finally stable brown yellow, while that in aqueous sodium hydroxide yields brown red changing to brown yellow and then to yellow stable for twenty-four hours. With alcoholic ferric chloride, the substance gives an olive green turning to olive brown colour. In concentrated sulphuric acid, the solid first turns orange-red and then dissolves to a yellow solution turning bright red. It gives a deep red colour with alcoholic *p*-benzoquinone solution. It is moderately soluble in all organic solvents. Colour reactions with alkaline buffer solutions of different p_H values ar e as follows: p_H 8·4, yellow, orange yellow and then deep red stable for 24 hours; p_H 9·0, yellow, orange red and then stable deep brown red; p_H 9·8, yellow rapidly changing to brown and then stable yellow. At lower p_H it seems to exhibit more attractive colours th an at higher p_H.

5 : 7 : 8-*Trihydroxy*-3 : 2′-*dimethoxy flavone* (*V b*)

For the preparation of O-3 : 2′-dimethyl datiscetin needed for this experiment, the procedure of Kalff and Robinson[7] was followed with the following modifications:

Methyl salicylate was methylated by boiling with two moles of dimethyl sulphate and excess of potassium carbonate in acetone medium till there was no ferric reaction. The product was washed with ice-cold sodium hydroxide to remove the last traces of unchanged methyl salicylate and then hydrolysed by boiling with 10% aqueous sodium hydroxide for half an hour. Thereby a pure sample of 2-methoxy benzoic acid could be obtained and it did not give any colour with alcoholic ferric chloride. When this pure sample of acid was used the resulting dimethoxy datiscetin came out crystalline even when it was crude, and not as a viscous brownish mass as given in the earlier report. One crystallisation from ethyl acetate-petroleum ether mixture was found to be sufficient to yield a pure product. For the preparation of the anhydride of O-methyl salicylic acid the use of thionyl chloride was found to be quite satisfactory.

Datiscetin dimethyl ether (1 g.) was dissolved in aqueous sodium hydroxide (0·5 g. in 50 c.c. of water) and cooled in ice. A solution of sodium persulphate (1·5 g.) in water (50 c.c.) was added drop by drop in the course of two hours. The product was worked up just as in the case of the oxidation of morin-3 : 2′ : 4′-trimethyl ether. 5 : 7 : 8-Trihydroxy-3 : 2′-dimethoxy-flavone (V *b*) crystallised from ethyl acetate as yellow rectangular prisms, melting at 250–1° with decomposition. Yield, 0·4 g. (Found: C, 61·7; H, 4·3; $C_{17}H_{14}O_7$ requires C, 61·8; H, 4·2%). It is moderately soluble in alcohol, benzene and acetone but sparingly so in ether and petroleum-ether. It dissolves in 5% aqueous alkali to a yellow solution immediately turning green. In aqueous sodium carbonate it dissolves with difficulty to yield a pale brownish yellow solution. With alcoholic ferric chloride it gives olive green colour rapidly changing to brown.

3 : 5 : 7 : 8 : 2′-*Penta-methoxy-flavone*

The above trihydroxy-dimethoxy flavone (V *b*) (0·5 g.) was methyalted by refluxing in dry acetone solution (150 c.c.) with dimethyl sulphate (0·7 c.c.) and anhydrous potassium carbonate (2 g.) for thirty hours. The product crystallised from benzene-petroleum ether in the form of colourless beautiful, stout rectangular prisms, melting at 140–1°. Yield, 0·5 g. It is insoluble in alkali, and gives no colour with ferric chloride (Found: C, 64·6; H, 5·4; $C_{20}H_{20}O_7$ requires C, 64·5; H, 5·5%).

3:5:7:8:2′-*Pentahydroxy-flavone* (8-*Hydroxy-datiscetin*) (*VI b*)

5:7:8-Trihydroxy-3:2′-dimethoxy-flavone (V *b*) (0·5 g.) was demethylated by boiling with hydriodic acid (d, 1·7; 10 c.c.) and acetic anhydride (10 c.c.) for thirty minutes. The product was worked up as usual. The crude 8-hydroxy datiscetin was dried in a vacuum desiccator and crystallised from ethyl acetate-petroleum ether mixture when it separated as small rectangular prisms melting at 283–4°. Yield, 0·15 g. (Found: C, 59·7; H, 3·5; $C_{15}H_{10}O_7$ requires C, 59·6; H, 3·3%). It dissolves in 10% sodium hydroxide solution to a deep orange red solution which fades rapidly. With 5% aqueous sodium carbonate it forms a yellow solution which rapidly changes to orange yellow, then violet and finally fades. It dissolves in saturated aqueous sodium bicarbonate to a yellow solution which rapidly changes to a permanent purple red solution. With alcoholic ferric chloride it gives an olive brown colour which changes to deep brown-red, and with alcoholic *p*-benzoquinone olive brown solution turning stable deep brown. In a buffer solution of 9·8 p_H it gives a yellow solution which first turns orange red and then purple red. It is moderately soluble in all organic solvents.

Remethylation of 8-*hydroxy-datiscetin*

8-Hydroxy datiscetin (VI *b*) (25 mg.) was methylated with dimethyl sulphate in excess using potassium carbonate and dry acetone. The product crystallised from benzene-petroleum ether mixture as elongated rectangular prisms melting at 141–2°. It did not give any colour with alcoholic ferric chloride and its mixed melting point with the synthetic sample of pentamethyl ether of 8-hydroxy datiscetin showed no depression. This clearly proves that isomerisation has not occurred during demethylation with hydriodic acid as in the case of similar flavones having no 3-hydroxy group.

7-*Hydroxy*-3:2′-*dimethoxy-flavone*-8-*aldehyde* (*VIII*)

7-Hydroxy-3:2′-dimethoxy flavone (VII *b*) (2 g.) was dissolved in glacial acetic acid (50 c.c.), hexamine (10 g.) added and the mixture refluxed on a wire gauze for six hours. The solution which was bright yellow in the beginning turned dark red; at the end of the period a mixture of concentrated hydrochloric acid and water (1:1, 30 c.c.) was added and the refluxing continued for another fifteen minutes. The solution was kept in a refrigerator overnight, when the aldehyde separated as a bright yellow solid. It was filtered, washed with water and crystallised from alcohol as colourless small rectangular prisms melting at 149–50°. Yield, 1 g. It dissolves readily in acetone and acetic acid but sparingly in alcohol and ether. It gives a fine red colour with alcoholic ferric chloride (Found: C, 65·6; H, 4·7; $C_{18}H_{14}O_6$ requires C, 66·2; H, 4·3%).

The 2: 4-dinitro-phenyl-hydrazone was prepared by boiling the compound with 2: 4-dinitro phenyl hydrazine hydrochloride in alcoholic solution for ten minutes. On recrystallisation from alcohol it melted at 298° with decomposition and appeared as orange coloured short needles under the microscope.

7: 8-*Dihydroxy*-3: 2′-*dimethoxy-flavone* (*IX a*)

The above aldehyde (VIII) (1 g.) was suspended in 6 c.c. of 2 N sodium hydroxide and enough pyridine added to dissolve it. The yellow solution was cooled in ice-bath and 6% hydrogen peroxide (7 c.c.) was added gradually during fifteen minutes with simultaneous shaking. The mixture assumed a deep reddish brown colour. It was left in ice-cold water for two hours with occasional shaking. On acidification with hydrochloric acid, a crystalline solid separated. It was collected and dried. More could be obtained from the mother-liquor by saturating it with common salt and extracting it with ether and evaporating the ether extract. The product crystallised from ethyl acetate and petroleum ether as aggregates of colourless short needles and rectangular prisms which sintered at 201° and melted at 204–5°. Yield, 0·6 g. It gives yellow solutions with concentrated sulphuric acid and 5% aqueous sodium hydroxide and a bright grassy green colour with alcoholic ferric chloride (Found: C, 64·8; H, 4·7; $C_{17}H_{14}O_6$ requires C, 64·9; H, 4·5%).

3: 7: 8: 2′-*Tetramethoxy flavone*

The above dihydroxy dimethoxy flavone (IX *a*) (100 mg.) was completely methylated by refluxing its acetone solution (30 c.c.) with dimethyl sulphate (0·2 c.c.) and freshly ignited potassium carbonate (1 g.) for twelve hours. The product was worked up as usual and it crystallised from ethyl acetate as colourless stout rectangular prisms melting at 119–20°. It does not give any colour with alcoholic ferric chloride (Found: C, 66·8; H, 5·4; $C_{19}H_{18}O_6$ requires C, 66·6; H, 5·3%).

3: 7: 8: 2′-*Tetrahydroxy-flavone* (*IX b*)

Dimethoxy-dihydroxy-flavone (IX *a*) was demethylated with hydriodic acid in the usual manner. It crystallised from acetone-ether mixture as tiny rectangular prisms, melting at 285–87° with decomposition (Found: C, 63·0; H, 3·9; $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%). This flavone gives a bright brown red colour with alcoholic ferric chloride, dissolves in concentrated sulphuric acid to a yellow solution and in aqueous sodium hydroxide and sodium carbonate to orange red solution. It is moderately soluble in most organic solvents but sparingly in petroleum-ether.

Summary

The methyl ethers of morin, resomorin and resodatiscetin have been made by different methods in order to examine the possible resistance of the 2′-hydroxyl group to methylation. No such resistance is found. 8-Hydroxy derivatives of morin, datiscetin and resodatiscetin have been prepared by employing methods of nuclear oxidation.

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